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ON THE GEOCHEMICAL MECHANISM CONTROLLING Ra-226 DISSOLUTION IN URANIUM MILL WASTES (TAILINGS)

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SUMMARY

In this research report, the results of laboratory experiments, operating mill data, and thermodynamic theory are used to evaluate the geochemical mechanism which controls the long-term dissolution of Ra-226 in U-mill tailings. This work does not examine the stability of Ra-226 in $BaSO_4(s)$ sludges. The fundamental hypothesis derived from earlier experiments is that radium exists in the solid phase as a coprecipitate with a host metal sulphate formed in the leaching tanks. The plausible host metals are calcium (gypsum), barium (barite), iron (jarosite), lead (anglesite) and strontium (celesite). Necessary conditions for formation of a coprecipitate are that the leaching pachuca liquor be supersaturated with respect the host crystal, that the thermodynamics of coprecipition be feasible, and that the kinetics of coprecipitation be sufficiently fast. One consequence of coprecipitation is that Ra-226 show a correlation with the cation of the host crystal when the host crystal dissolves.

Acid digestion experiments were made on ore samples from Elliot Lake in the laboratory with perchloric acid, nitric acid, and sulphuric acid at 25°C and 60°C. Dissolution studies were made with various sequestering solutions (EDTA, KCl, $FeCl_3$, $CaCl_2$, $BaCl_2$, $HClO_4$, H_2SO_4, HNO_3; 10^{-5} to 10^{-1} M) mainly on leaching pachuca solids, but also on Lacnor and Gunnar tailings and old Nordic tailings. The tailings and leaching pachuca solids are all from sulphuric acid leaching processes. The results of acid digestion experiments on the ore, leaching liquor data from the mill, and chemical dissolution studies on the solids (leaching pachuca solids, tailings) indicate that Ra-226 behaviour is correlated only with barium and lead behaviour. The leaching-tank and laboratory acid-digestion data indicate that the solutions are supersaturated only with respect to barite ($BaSO_4(s)$), gypsum ($CaSO_4.2H_2O$), and anglesite ($PbSO_4(s)$). Incorporation of these data into the thermodynamic theory for radium coprecipitation with various metal sulphates indicates that the amount of Ra-226 dissolved compared to the amount of lead dissolved is above the equilibrium capacity of $PbSO_4(s)$. But the ratio of Ra-226 dissolved to barium dissolved is only 20-30% of the capacity of $BaSO_4(s)$. This suggests that a host barium sulphate solid contains most of Ra-226 as a coprecipitate with lead sulphate containing the remainder.

It is postulated that Pb-210, Po-210 and Ra-228 behaviour in the leaching tanks is also controlled by dissolution and resorption by coprecipitation onto the solids of the leahing tanks. The amount of Pb-210, Po-210 and Ra-228 observed in solution in the leaching tanks together with a discussion of the minerology of Pb and Ba in the ore are used to argue qualitatively that most of the Ra-226 coprecipitates with $BaSO_4(s)$ and the remainder with $PbSO_4(s)$. Further measurements on existing laboratory solutions are required to complete these qualitative arguments. Further experiments with other extraction agents with greater chemical selectivity than those used in this study are required to differentiate the degree to which Pb and Ba control Ra-226 dissolution.

Coprecipitation theory could be used directly to evaluate the data of this report. But its application to dissolution data is a novel application because the theory is normally applied to precipitate formation, not to precipitate dissolution. Futhermore the theory is applied to solutions supersatured with respect to, or minimally at equilibrium with, the host crystal, whereas the solutions in these dissolution studies were undersaturated with respect to the host crystal ($BaSO_4(s)$; $PbSO_4(s)$. The theory requires further evaluation before it can be applied to the data of this report.

An adsorption study was conducted in acid solutions representative of the leaching tanks. Its results indicate that Ra-226 does not significantly adsorb on leaching pachuca solids at pH less than 1 in nitric acid solutions but that it significantly "sorbs" in sulphuric acid solutions. This "sorption" with a K_D varying from 150 ml/gm at a solid:liquid ratio of 1:40 to 1 ml/gm (solid:liquid ratio = S:L = 1:1) is hypothesized to be due to the coprecipitation of Ra-226 with barium sulphate, rather than reversible sorption of Ra-226 onto the solid phase. A hypothesis to explain the variation of K_D with solids concentration is given.

Surface analytical techniques (SIMS, ESCA, Auger, SEM, Mossbauer) have been applied to the surface of the leaching-pachuca solids and to the tailing samples. The objective of this work was to identify the possible solids containing Ra-226. They show small precipitates on the surface of the tailings of a thickness of 1-2 um. With Mossbauer, the presence of jarosite in tailings has been identified, but not in the leaching-pachuca solids. The depth profiles with SIMS present interesting data, but an average over several particles is exhibited due to the 50-150 um beam used. Further work is required in order to identify the location and morphology of $BaSO_4(s)$ and $PbSO_4(s)$ containing Ra-226.

For the NUTP source term model, it is suggested that Ra-226 dissolution be modelled as controlled by barium sulphate and by lead sulphate host crystals. This would involve using equilibrium data to describe solid-solution relationships of these precipitates, and the lambda (Doerner-Hoskins) distribution coefficient to model the association of radium with each solid. A minor fraction of Ra-226 dissolution behaviour (less than 0.1%) would be described by its coprecipitation with gypsum. The relative proportion of Ra-226 in barite and anglesite is a calibration parameter not resolved by this research. The data of this report can be developed to give parameter distributions for the ratio of Ra/Ba and Ra/Pb for incorporation into the probabilistic assessment. Further analysis is required to complete this development.

Several areas require further laboratory work. They include measurements on existing laboratory solutions used in this project. The reason why laboratory solutions remain supersaturated with respect to barite and anglesite for at least a month need to be explored to justify use of equilibrium conditions for long-term, source term modelling.

In the long-term, several steps will form the basis for substantiating or modifying, and mathematically describing the mechanisms postulated in this research (Figure 3.1). They include:

(i) Identify the minerals from which radium, lead, barium, and other elements of concern are derived, using standard mineralogical and micro-mineralogical techniques.

(ii) Identify the solids formed, the species in solution, their mineralogical sources, and the concentrations of each over time as the ore dissolves.

(iii) Identify the fate of each of these solids and species in the process stream.

(iv) Identify the surface precipitate (host crystal) containing Ra-226 and Ra-228 with direct observational techniques and identify the crystallization site.

(v) Evaluate and quantify the kinetics of dissolution of mono-minerals containing Ra-226, Ra-228, Ba, Pb, Ca, Fe and Sr.

(vi) Numerically simulate these coprecipitation kinetics using data from simple laboratory systems to evaluate Ra-226/Ra-228 differences.

(vii) Evaluate steps (v) and (vi) in the heterogeneous mill system.

(viii) Couple steps (v), (vi) and (vii) with an evaluation of supersaturation conditions in the mill of the relevant parent crystal.

(ix) Validate that the same host solid controlling Ra-226 in the leaching pachua solids also controls its dissolution behaviour in old tailings.

(x) Trace the fate of each of the solids and soluble species in the mill processing streams from the time of placement of the tailings behind their containment structure, to the present.

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1.0 INTRODUCTION

Radium-226 is a radionuclide leaching from uranium mill waste (tailings) which is of prime concern to environmental managers. It has a major influence upon the radiological dose to man resulting from uranium mill tailings (Snodgrass et al., 1982; Lush et al., 1983; NEA, 1983). Despite many laboratory and field studies, the geochemical mechanism which controls the leaching (dissolution) behaviour of radium-226 has remained unclear. It is essential that the geochemical mechanism that controls the Ra-226 leaching behaviour be understood to permit the sound, long-term environmental and engineering management of uranium tailings.

2.0 PREVIOUS WORK

Past work by others (e.g, Skeaff, 1977) has established that Ra-226 essentially remains on the solid phase in the leaching tanks of the mill, whereas other radionuclides of the U-238 chain (i.e., U-238, Th-230, Pb-210) are dissolved by acid leaching. Using the chemical idea that acid (sulphuric acid) attack upon the uranium minerals should break uranium and all of its daughters out of the parent U-238 crystal structure, it is expected that Ra-226 should enter solution in proportion to the amount of U-238 dissolved from the uranium mineral. For radionuclides in secular equilibrium, an equivalent radioactivity to that of the parent is expected. One can question whether the uranium is sufficiently attacked by acid leaching to liberate Ra-226. But the work of Skeaff (1977) shows that the percent of Ra-226 in the -200 mesh fraction increases from 50-60% in the raw ore to approximately 80% after the first leaching tank. Thus, it is clear that much of the Ra-226 has been dissolved from coarser material and redistributed to the finer material. This infers that it must enter solution and then be "resorbed" onto the solids.

The most plausible possibilities for explaining this solid form of radium are that it is either on the surface of the leached solids in a "reversibly absorbed" state, or as a "coprecipitate" with a metal sulphate precipitate. Solids from different parts of the mill (leaching tanks, neutralization tanks) have been analyzed previously using scanning electron micrograph-Xray emission techniques (SEM-XRE; Constable and Snodgrass, 1984; Snodgrass et al., 1983c). These studies demonstrate that small quantities of surface precipitates are found on solids leaving the leaching tanks and that substantial additional amounts of precipitates are found on solids leaving the neutralization tanks. The coatings formed in the leaching tanks could either "cover" reversibly absorbed Ra-226, effectively cementing it to the surface, or could be the location of a precipitate containing Ra-226 as a coprecipitate. This SEM-XRE analysis suggests that such a precipitate must be quite small (less than 1 micron length scale on the surface of 0.5 mm diameter solids).

Previous laboratory work using chemical techniques has produced a confusing picture of geochemical controls on Ra-226 behaviour; variables examined include liquid-to-solid ratio, concentration of cations and anions and other leaching agents in solution, ionic size and charge of the cation, and surface area of the solid (e.g., Wiles, 1978; Seeley, 1977; Benes, 1982; Benes et al., 1982; Nathwani and Philips, 1979a, 1979b; Nixon et al., 1982;

Ryan and Levins, 1980; Yagnik et al., 1981; Levins et al., 1978). Recent work (Nirdosh et al., 1984; Shoesmith, 1984) has systematically described all these different experimental variables and made some observations concerning the effect of alternative chemical techniques on leaching Ra-226 from mill solids, but does not allow general conclusions concerning which mechanism is dominant. Another literature review (Benes, 1984) suggests that dissolution of a radium-barium sulphate coprecipitate may control much of Ra-226 found in tailings. Benes (1982) measured complexation reactions of Ra.

Previous work (Snodgrass et al., 1983c; Constable and Snodgrass, 1984) has suggested that Ra-226 coprecipitation with barium sulphate is the controlling host precipitate. This is based on four pieces of evidence:

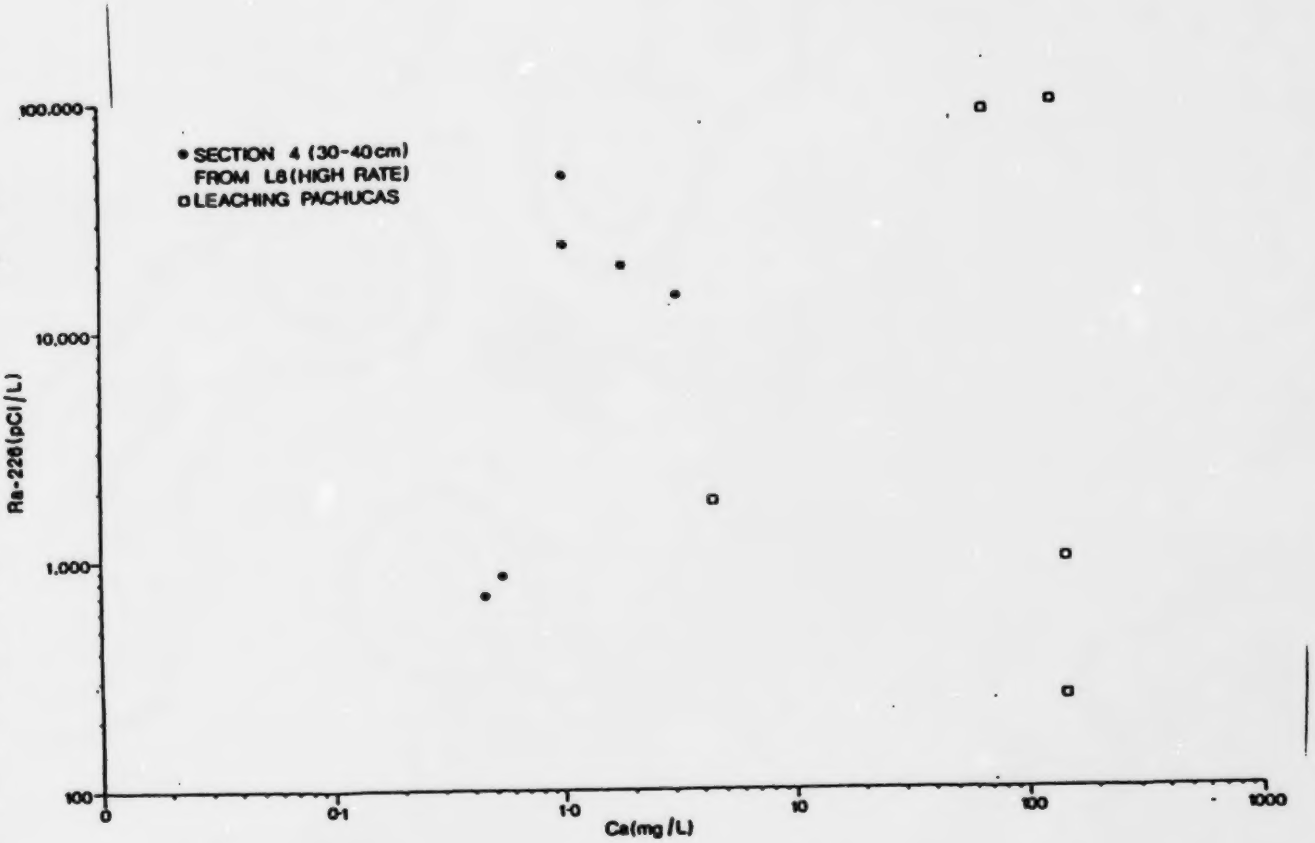
- of the several plausible metal sulphates or hydroxides (Ca, Pb, Fe, Ba) with which Ra-226 may coprecipitate , barium is the only metal which shows a consistent correlation with Ra-226 in studies using KCl and EDTA as the leaching agent on uranium mill (leaching pachuca) solids and on 30 year old tailings (compare Figure 2.1a to 2.1d);

- in the lysimeter leachate from the 30-year old tailings, barium is close to equilibrium with its solid sulphate form;

- in one lysimeter where pyrite was completely consumed in the surface 10 cm, 80% of the Ra-226 had leached from this section; this suggests that when pyrite oxidation is complete such that sulphate concentrations in the pore water are quite low, a sulphate mineral containing Ra-226 will dissolve; and

- chemists argue that Ra-226 can easily substitute into the crystal lattice of the $BaSO_4$ without substantially affecting its lattice parameters due to the similarity of charge and ionic radius of Ba and Ra-226.

FIG. 2.1a Scattergram from washing experiment of Ra-226



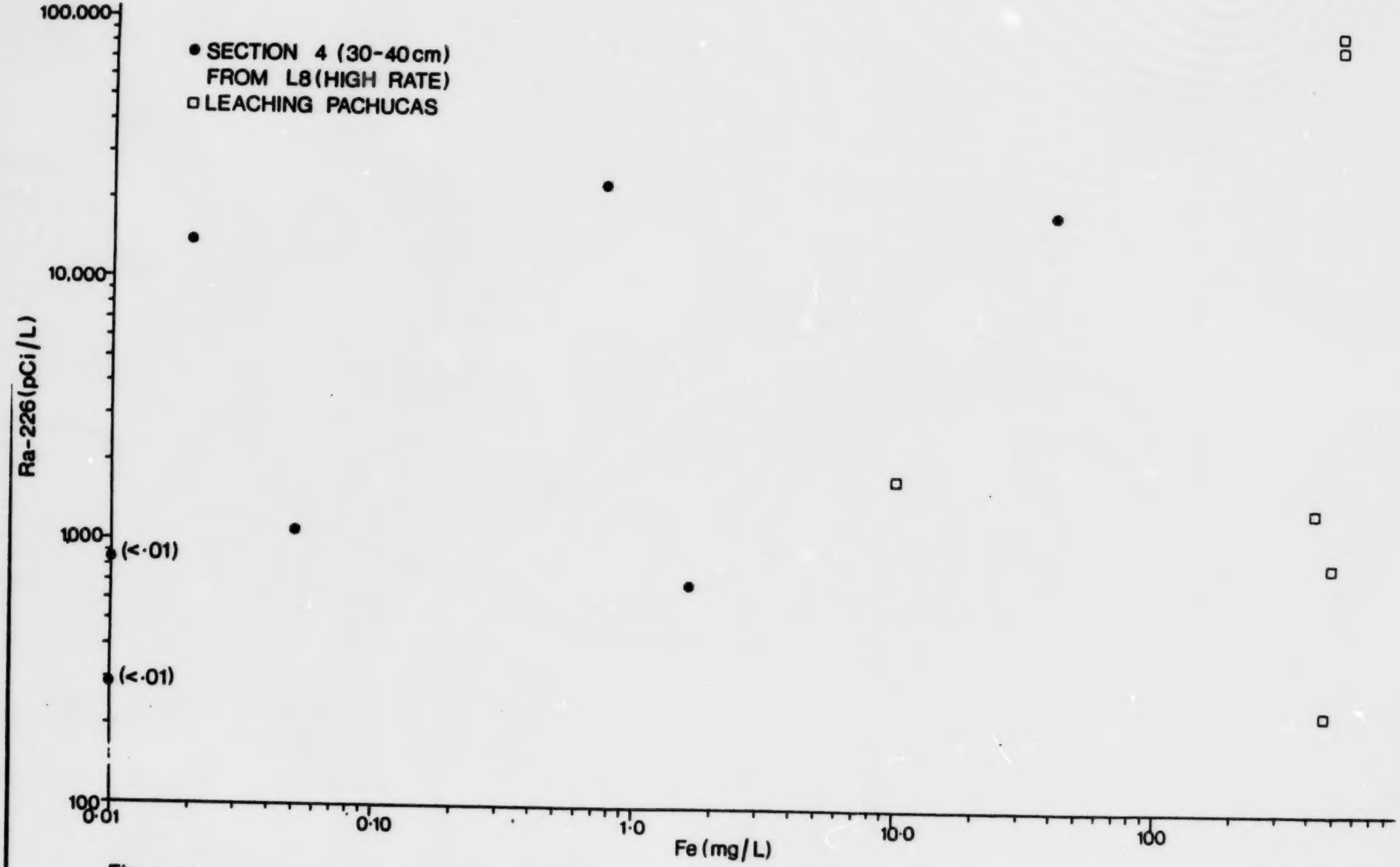


Fig. 2.1b Scattergram from Washing Experiment of Ra-226 versus Iron

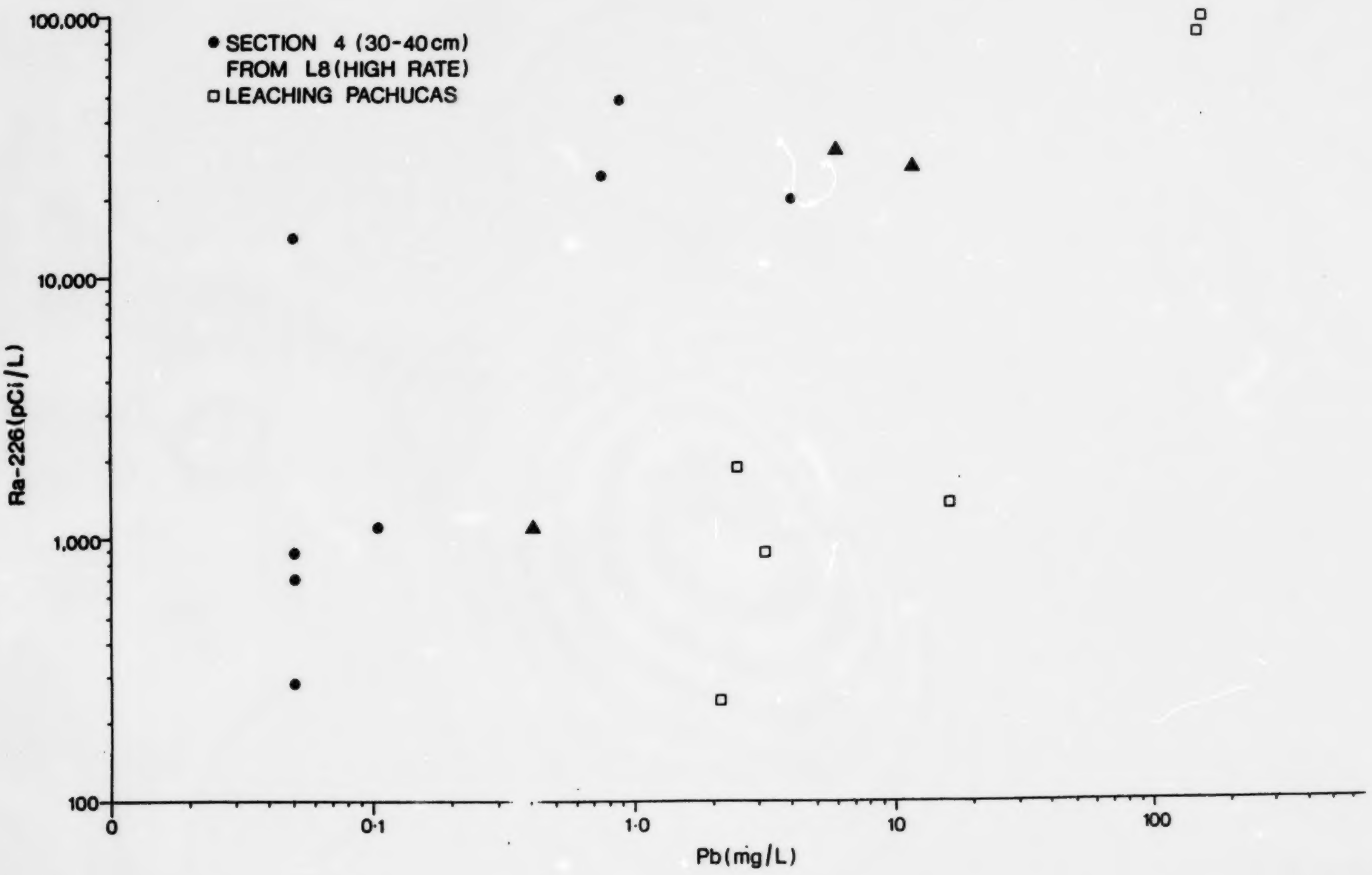
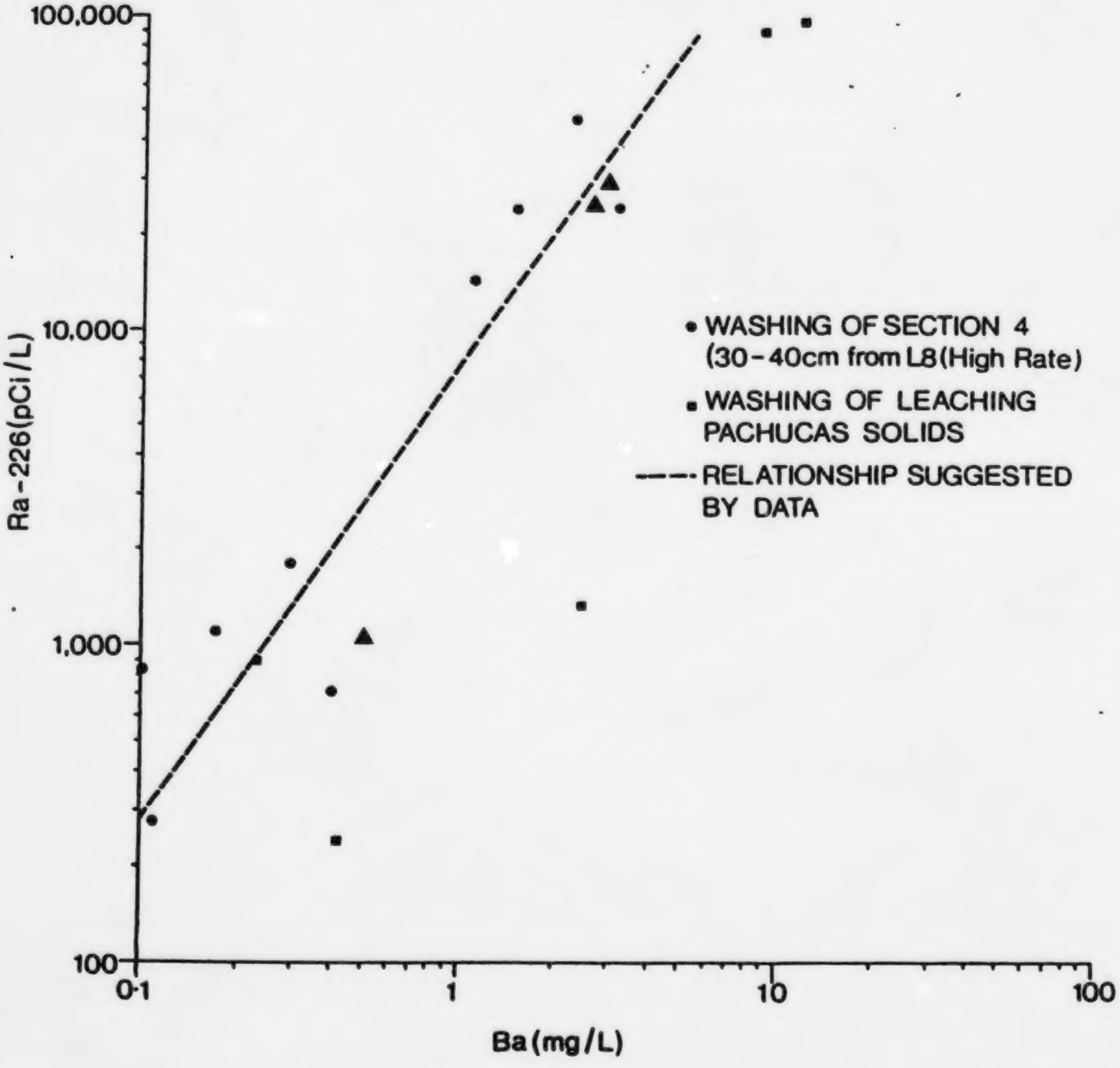


Fig. 2.1c Scattergram from Washing Experiment of Ra-226 versus Lead

FIG. 2.1d Scattergram from washing experiment of Ra-226 versus Barium



The key piece of evidence to us is the correlation between Ba and Ra-226 (Figure 2.1d from Constable and Snodgrass, 1984) versus the lack of relationships between Ra-226 and three metals (Fe, Ca, Pb, Figures 2.1a, 2.1c, and 2.1b from Constable and Snodgrass, 1984). This is supplemented by the results of equilibrium calculations showing the theoretical possibility for the leachate waters being near to equilibrium with respect to $BaSO_4$.

The objective of this report is to present theoretical and experimental evidence to further eludicate the geochemical mechanism which controls the dissolution behaviour of Ra-226 in U tailings piles. The work particularly examines whether a lead sulphate or barium sulphate coprecipitate controls Ra-226 dissolution. It also examines the role that adsorption plays in controlling Ra-226 dissolution.

3.0 CONCEPTUAL MODEL OF MECHANISMS INVOLVED IN Ra-226 DEPOSITION AND SUBSEQUENT DISSOLUTION

The hypothesis tested in this work is that a metal-sulphate coprecipiatate is the main solid form of Ra-226 in tailings resulting from sulphuric acid milling and that this coprecipitate is formed in the first several leaching tanks. The formation process is kinetically controlled. A conceptual diagram of the hypothesis and of the mechanisms involved in Ra-226 deposition in the leaching tanks is shown in Figure 3.1 and described in Section 3.1. A conceptual diagram of how Ra-226 dissolves subsequently, is given in Figure 3.2 and discussed in Section 3.2.

3.1 Leaching Tank Processes

The method by which formation of this coprecipitate may occur is sketched in Figure 3.1. In the leaching tanks, a mixture of uranium and other minerals is introduced into a sulphuric acid solution at 55-60 °C. The acid (H^+) attacks uranium-containing minerals (e.g., UO_2; Figure 3.1), thorium-containing minerals (e.g., Th-232 in monazite), sand (SiO_2; Figure 3.1), and other solids. The acid attack on the uranium and thorium minerals should liberate the same activity of U-238 and its daughters, and of Th-232 and its daughters provided that (i) secular equilibrium exists in the parent mineral and (ii) adsorption or coprecipitation of the liberated radionuclides back onto the solids does not occur. The actual activity of U-238 liberated will normally differ from that of Th-232, depending upon their relative abundance, and their dissolution kinetics.

Analysis of the data gathered in this project from the leaching tanks of Rio Algom (Nordic mine; see Table 3.1) indicate that approximately 50% of Th-230, 0.1-0.3% of Ra-226, 4% of Pb-210 and 4% of Po-210 are observed in solution when the activity of U-238 in solution is used to define the expected level of its daughters in solution. Using Th-232 solution activity to define an expected level of its daughters in solution, less than 10% of Ra-228 but 100% of Th-228 are observed in some leaching solutions and in the acid digestion experiment (see Section 6.1). These data suggest that most of the Ra-226, Ra-228, Pb-210 and Po-210 expected in solution either must not leave the host mineral during leaching or must be reprecipitated or adsorbed.

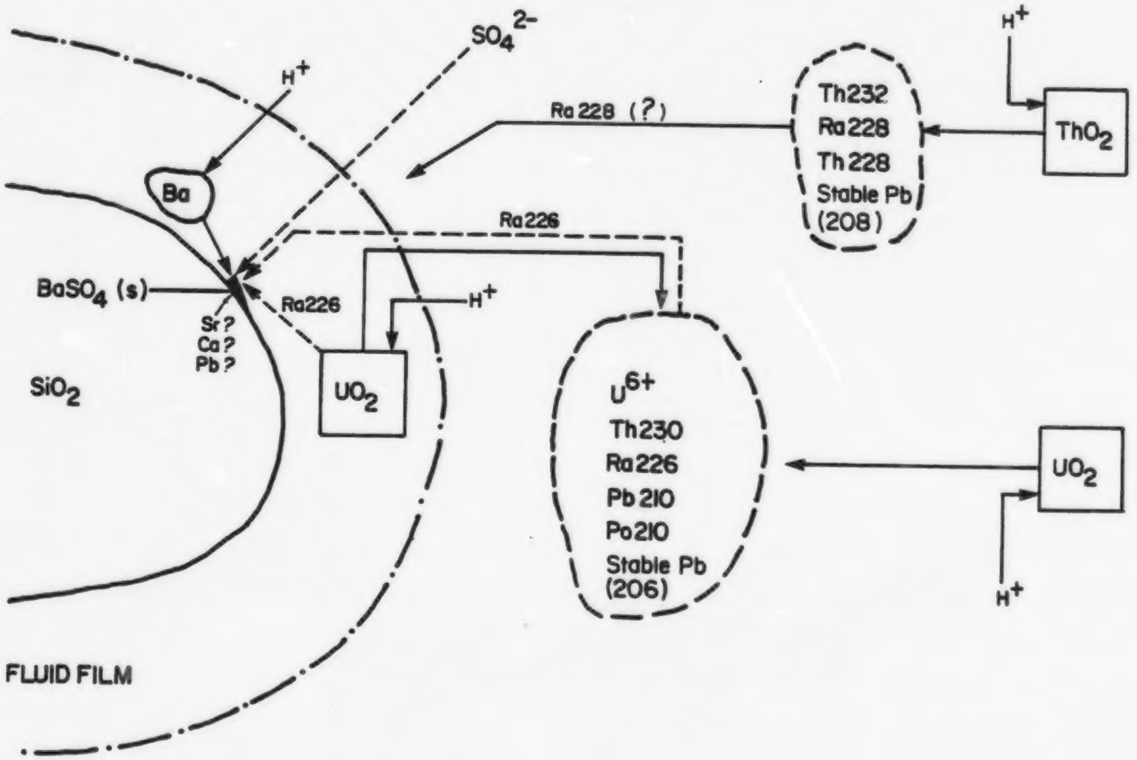

H+
SO4 2-
H+
Ra 228 (?)
Th232
Ra228
Th 228
Stable Pb
(208)
ThO2
Ba
Ra226
BaSO4 (s)
Sr?
Ca?
Pb?
Ra226
H+
SiO2
UO2
U6+
Th230
Ra226
Pb 210
Po210
Stable Pb
(206)
UO2
H+
FLUID FILM

FIGURE 3.1 Conceptual Model to be Tested

TABLE 3.1

ACTIVITY OF RADIONUCLIDES IN RIO-ALGOM LEACHING PACHUCAS
(Bq/L)

Radionuclide	Dec./84 Tank 12	Dec./84 Tank 12	Jan./85 Tank 1	Jan./85 Tank 12	Feb./85 Tank 1*		Feb./85 Tank 3*	Feb./85 Tank 5*	Feb./85 Tank 7*	Feb./85 Tank 11*	Feb./85 Tank 12*	Sept./85 Tank 1+	Sept./85 Tanks 12+	
					First Analysis	Second Analysis							Dupl. 1	Dupl. 2
U-238 (mg/L)	1600	1800	-	2150	2100	1800*	2200	2800	2100	2100	1900	2400	2400	2800
Th-230 (Bq/L)	9710	9910	-	8660	9820	13230*	12800	13480	12850	13500	12510	12020 (14600)*	14400 (15900)**	7800 (15500)**
Ra-226 (Bq/L)	63.4	68.7	12.1	13.1	2.66	–	2.39	26.3	25.7	23.6	19.	56.	37.	54.
Pb-210 (Bq/L)	629	619		623	926	930*	870	950	750	600	620	1390	630	628
Po-210 (Bq/L)	419	347	-	290	438	-	-	-	-	-	-	506	390	384
Th-232 (Bq/L)	1157	794	-	397	1730	1950*	1560	1900	1930	1750	1760	1920 (2800)**	2320 (2380)**	1160 (2060)**
Ra-228 (Bq/L)	LT 100	LT 100	-	700	2980*	-	2340	3490	3330	2810	2640	1180	1150	918
Th-228 (Bq/L)	1157	794	-	1760	1950	1940*	1550	2100	2050	1740	1940	1910 (2800)**	2316 (2380)**	1154 (2060)**

LT = less than

* Sample was filtered immediately after sampling and diluted 1:10. First analysis for Feb./85:Tank 1 was made in early March, 1985; the second analysis was made in early September, 1985. The two analysis are blind replicates.

+ Sample was filtered immediately after sampling and diluted 1:2. Duplicate samples were formed by taking original sample, mixing well, dividing into two different samples and submitting to laboratory as a blind replicate.

** A second analysis was requested after receipt of first results.

According to process operators, about 95 to 98% of the uranium is brought into solution. Thus, it is difficult to see how a significant proportion of Ra-226, Pb-210, and Po-210 would remain in the residual uranium mineral. Accordingly, resorption defined as including reversible adsorption and coprecipitation, is the most plausible explanation for these observations in Table 3.1.

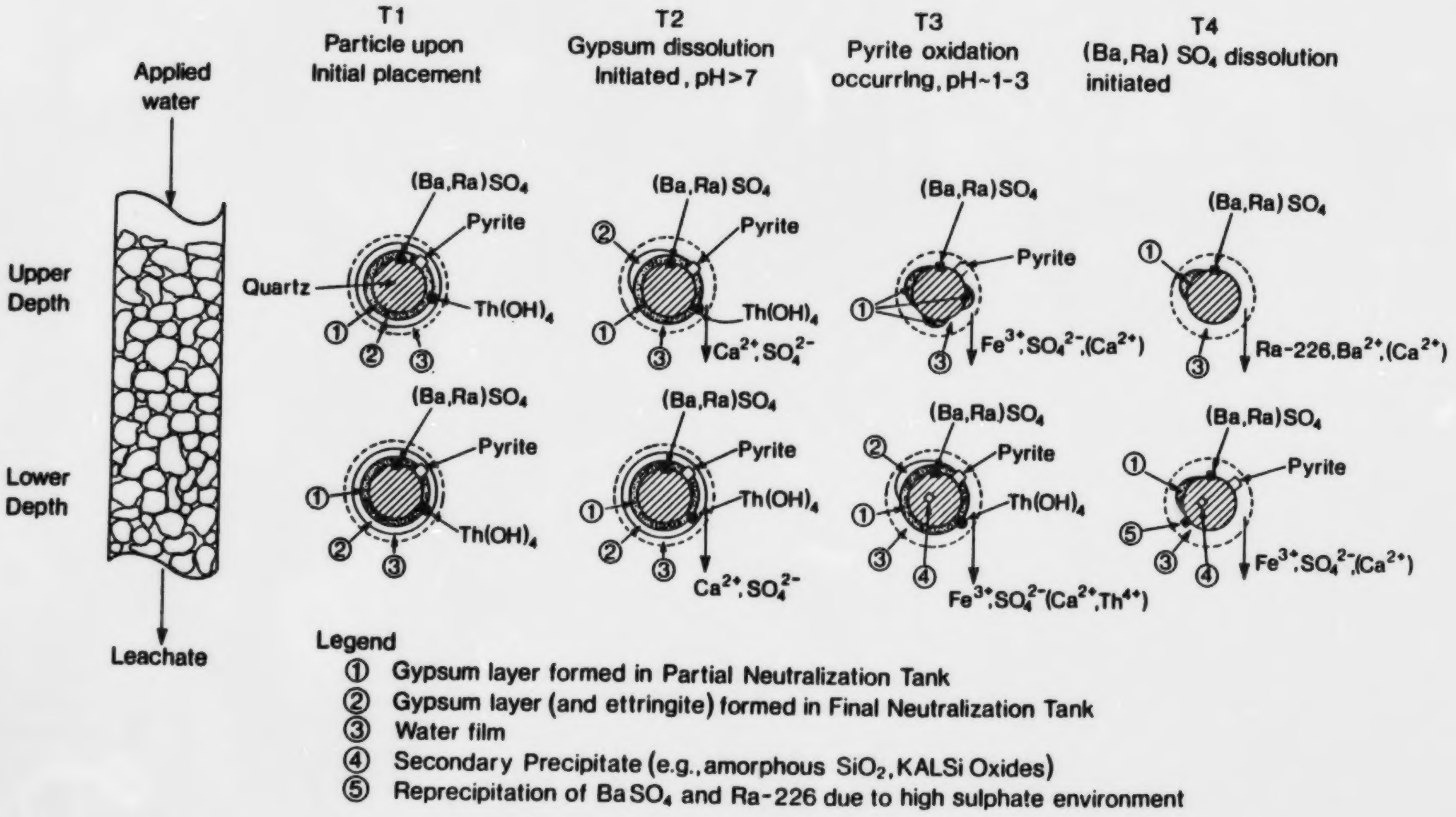
It is our hypothesis that the following steps are involved. Proton attack on the uranium and thorium minerals liberates the parent and daughter radionuclides into solution. Proton attack also liberates stable lead from the U-238 mineral along with barium, strontium and calcium from other minerals containing them in trace amounts. If conditions are appropriate, the metal ions and/or sulphate ion will absorb to a surface such as a silica surface. If the local geometry (on the order of a few square angstroms) is appropriate, crystal growth will be initiated. Figure 3.1 suggests that barium sulphate growth on a silica surface with Ra-226 coprecipitation is the method for radium removal from solution and that strontium, calcium, and lead sulphate are also plausible metal sulphates for coprecipitating of radium-226 from solutions.

Figure 3.1 suggests that Ra-226 can migrate from an uranium mineral located within the fluid boundary layer around the silica mineral or from bulk solution. In addition, barium may migrate within the fluid boundary layer or from bulk solution. Sulphate will generally migrate from bulk solution. Evidence that barium may originate from minerals located only in the fluid boundary layer is provided by SEM-XRE results which indicate that various mill solids of the order of 5 um (e.g., aluminosilicates) and smaller are attached (cemented) to host quartz solids. Evidence that various metals will originate from bulk solution is provided by the size of minerals after balling; for example, uranium and thorium minerals are ground to sizes of the order of 20 um and larger. The thickness of fluid films (the laminar sublayer) which affect transport is expected to be approximately 10 um in such a turbulent environment as in the leaching pachucas. Hence, transport both from bulk solution and through the fluid film to the nucleation site is the most probable sequence of steps.

3.2 Overview of Geochemical Processes in Tailings

A conceptual model of the evolution of the tailings through time is given in Figure 3.2. The time history of the example is divided into 4 different phases: (i) tailings

FIGURE 3.2 CONCEPTUAL MODEL OF THE EVOLUTION OF TAILINGS


T1
Particle upon Initial placement
T2
Gypsum dissolution Initiated, pH>7
T3
Pyrite oxidation occurring, pH~1-3
T4
(Ba,Ra) SO4 dissolution initiated
Applied water
Upper Depth
Lower Depth
Leachate
Quartz
(Ba,Ra)SO4
Pyrite
Th(OH)4
①
②
③
④
⑤
Ca2+, SO42-
Fe3+, SO42-, (Ca2+)
Ra-226, Ba2+, (Ca2+)
Fe3+, SO42- (Ca2+, Th4+)
Legend
① Gypsum layer formed in Partial Neutralization Tank
② Gypsum layer (and ettringite) formed in Final Neutralization Tank
③ Water film
④ Secondary Precipitate (e.g., amorphous SiO2, KALSi Oxides)
⑤ Reprecipitation of BaSO4 and Ra-226 due to high sulphate environment

characteristics upon placement and the mill processes which control these characteristics, (ii) tailings processes during gypsum dissolution but before acidification starts, (iii) tailings processes during pyrite oxidation, and (iv) tailings processes after completion of pyrite oxidation in surface layers.

When milled solids leave the mill (Time T1), they are coated with three different forms of precipitates (or layers). These precipitates are formed in the leaching pachucas, the partial neutralization tank and the final neutralization tank. In the leaching pachucas, uranium, thorium, Ra-226 and Pb-210 are leached along with various metal sulphides. The reduced metals are oxidized and metal sulphates precipitate. The $(Ba, Ra)SO_4$ precipitate is shown as occurring as part of the first inner most layer.

Ra^{2+} forms $RaSO_4^{\,o}$ complexes and is rapidly incorporated into a $BaSO_4(s)$ structure. For solution concentrations of 100 pCi/L of Ra-226 and 1 mg/L of Ba^{2+}, the ratio of Ra-226 to Ba is approximately 10^{-6}. Accordingly, in such solutions, the number density of Ra-226 incorporated into the $BaSO_4(s)$ lattice is so small that significant effects upon crystal growth of $BaSO_4(s)$ due to Ra-226 incorporation are probably small. Because the molecular sizes of Ra^{2+} and Ba^{2+} are quite similar, significant effects upon crystal growth would occur only when the molar ratio of Ra-226/Ba^{2+} is much larger.

Thorium species released in the leaching pachucas are expected to be carried through the mill until the final neutralization tank. Thus, they are expected to be in the outer layer. Pb-210 will form sulphate complexes and may coprecipitate with $PbSO_4(s)$ in the leaching pachucas. The number concentration of $PbSO_4$ complexes may increase as the water flows into the partial neutralization tanks because the number concentration of $SO_4^{\,2-}$ ions increases relative to the decrease of the number concentration of $HSO_4^{\,-}$ ions as the pH is raised. A $(CaPb)SO_4$ coprecipitate may also form. Some thorium is expected to precipitate or absorb in the partial neutralization tank because of the increase of pH. Most of the thorium species are postulated to precipitate in the final neturalization tanks as hydroxides, or to become enmeshed in the gypsum-ettringite (Ca-S) precipitates.

All precipitates can be viewed as forming in successive layers. The total layer is only a few microns thick. While the precipitates are conceptualized herein as being in layers, they are in fact, a fairly porous structure with interwoven rods, dendrites and polygons.

Pore spaces are readily discernable from SEM pictures of tailings. If the precipitates do not dissolve in the tailings pile, they significantly increase the tailings particulate surface area compared to the surface area of the host quartz solids. Furthermore, because of incomplete covering of the quartz solids, the layers have irregular thicknesses (from nil to substantial thickness). The precipitates coat individual small particles (e.g., alumino-silicate plates) and help "cement" these small particles to the larger coarser quartz solids formed by the milling of the mined silica-ore solids. Disposal of the final neutralization tank slurry to the tailings pond/pile allows the agglomerations of small, less dense particles to separate from larger, denser quartz tailings.

In addition to sequential deposition of gypsum creating "conceptual" layers, the radium distribution in the host barium sulphate will also be layered. While it is possible that radium-226 would be uniformily distributed throughout the host crystal, it is doubtful because of the rapid kinetics of precipitation. This is often described by the field of coprecipitation chemistry as the onion ring. In the analogy, successive rings of barium sulphate are precipitated with different densities of Ra-226 in each ring. The ring character is caused by the kinetics of precipitation. The distribution of Ra-226 in the solid is described by the lambda (Doerner-Hoskins) kinetic distribution coefficient.

On placement in the tailings pile, available data suggest that the leaching waters remain basic for a period of time. The main constituent of dissolved solids during this period is gypsum. Dissolution of gypsum should give a pH of about 7. Because the observed pH is often higher, residual buffering from mill-added lime influences the pH. During the time period of gypsum dissolution, Ra-226 enmeshed within the $CaSO_4$ precipitates is the plausible source for Ra-226 in the leachates.

During this dissolution process (Time T2, Figure 3.2) it is postulated that the $Th(OH)_4$ solids originally enmeshed within the gypsum in the final neutralization tank remain on the particles until the pH decreases sufficiently to initiate their dissolution.

When sufficient gypsum has dissolved, pyrite grains are exposed to dissolved oxygen and to the organisms in the film water covering the solids (Time T3, Figure 3.2). Also, some pyrite grains may be bare because final neutralization prcipitates did not cover their surface. Atmospheric oxygen penetrating to various depths of the unsaturated zone between rainfall events is the main source for oxygen in the tailings waters. Biofilms containing T. ferrooxidans develop. The actual origins of such bacteria are not clear but microbiological work (e.g., Ritcey and Silver, 1980; Constable and Snodgrass, 1984) demonstrate that pyrite oxidizers develop both in tailings fresh from the mill and in old tailings which are dried and then leached.

As pyrite oxidation develops, the pH starts to decrease. It is suggested that pH is maintained in the 5-7 range as the pyrite-oxidizer community develops and as residual buffering minerals are attacked. As the pH decreases, the concentration of sulphate increases and minimizes the dissolution of gypsum. This sequence maintains the presence of gypsum in the solid phase of the unsaturated zone until the completion of pyrite oxidation.

In older tailings, the precise source of all Ra-226 in solution is unclear. But it is probable that it results from dissolution of residual gypsum, oxidation of residual uranium minerals and equilibrium exchange of the barium sulphate with solution. Release of adsorbed Ra-226 is also possible, albiet adsorption probably constitutes a small portion of Ra-226 released at pH 2 and lower due to a competition for adsorption sites between Ra-226 and hydrogen ion.

When pyrite oxidation is nearly complete, the pore water sulphate concentration will decrease because the rate of sulphate production decreases. This allows the host crystal containing Ra-226 on the quartz mineral particles to begin to dissolve due to the low sulphate concentration in the pore water (Time T4, Figure 3.2). This occurs at the top of the tailings. In one lysimeter experiment (Constable and Snodgrass, 1984), 80% of Ra-226 dissolved over 1.5 years in the top 10 cm of tailings, but the Ra-226 appears to have reprecipitated in lower depths of the tailings because little of the mass of Ra-226 left the tailings. Reprecipitation is probable. It is suggested that local variations in deeper zones of the tailings provide large enough concentrations of sulphate in the pore water deeper in the tailings to prevent continuous dissolution of $BaSO_4(s)$ and to cause precipitation of barium and Ra-226 migrating from the upper zones.

4.0 RELEVANT ASPECTS OF COPRECIPITATION THEORY

4.1 General

A review of the theory of coprecipitation and of other similar mechanisms (codeposition, entrapment) is given in the appendix in general terms and for barium (radium) sulphate in particular. This review is summarized in this section and amplified by more recent work (Riese, 1983; Langmuir and Riese, 1985).

The chemistry of coprecipitation involves formation of the host solid (precipitate) and the entrapment of the "trace" element within the parent solid. A coprecipitate will form when the solution is undersaturated with respect to the trace element but supersaturated with respect to the host mineral and where the host mineral (crystal) has an affinity for the trace element. Hence, the necessary conditions to form a coprecipitate are that the leaching pachuca liquor be supersaturated with respect to the host cyrstal, and that the thermodynamics and kinetics of coprecipitation be feasible. This means that Ra-226 show a correlation with the cation of the host crystal when the host crystal dissolves.

Some of the first fundamental work on nucleation and crystal growth was conducted on barium sulfate (Nelsen, 1957, 1958, 1961, 1967; Peters et al., 1966, 1968, 1969). Some of the first fundamental work on coprecipitation theory was conducted on (barium, radium) sulfate (Gordon and Rowley, 1957; Gordon et al., 1959). This has resulted in the crystal growth theory for (Ba, Ra)SO_4 being fairly well developed. More recently, work has centred on extending the theory for coprecipitation to other sparingly soluble salts, and to oxides, hydroxides and sulphides of various cations.

Two principal theories have evolved: The Berthelot-Nernst theory also called the Henderson-Kraczek theory (O'Nions and Powell, 1977), and the Doerner-Hoskins (1925) theory. The Berthelot-Nernst theory is also known as the homogeneous (D) distribution law while the Doerner-Hoskins theory is also called the logarithmic (or lambda: λ) distribution law.

The homogeneous (D) distribution law is applicable to equilibrium reactions. The logarithmic (λ) distribution law is applicable to reactions not at equilibrium.

Under equilibrium conditions, it is assumed that the whole crystal is at equilibrium with the solution composition. This means that the trace element is homogeneously distributed throughout the whole crystal.

Under kinetic conditions, only the surface layer of the crystal is at equilibrium with the solution. Thus, the crystal has a layered distribution with each layer having its own concentration of the trace element. This layer distribution is often described by analogy to an onion with each "onion ring" having a different trace element composition. This ringed structure can form in a batch reactor where precipitation of the host crystal is initially rapid and then becomes progressively slower due to lower degrees of supersaturation over time. A ringed structure may also result in leaching tanks in series in which dissolution of barium from its host mineral and of Ra-226 from the uranium-containing minerals progress at different rates.

The D and λ models are expressed mathematically as follows for the crystal-solution reaction:

$$A^{n+} + MX = M^{n+} + AX \qquad (4.1)$$

Here A^{n+} is the trace element cation undergoing coprecipitation
M^{n+} is the parent cation in the crystal (like charge to A)
X is the parent anion in the crystal
MX is the parent crystal
AX is the resultant mixed crystal (containing A in MX)

For coprecipitation of Ra with Ba, the reaction becomes:

$$Ra^{2+} + BaSO_4(s) = RaSO_4(s) + Ba^{2+} \qquad (4.2)$$

For coprecipitation of Ra with Pb, the reaction is written as:

$$Ra^{2+} + PbSO_4(s) = RaSO_4(s) + Pb^{2+} \qquad (4.3)$$

In both cases, $RaSO_4(s)$ refers to the (Me, Ra) SO_4 mixed crystal solid as opposed to a radium sulfate solid. "Me" in the formula, (Me, Ra) SO_4, refers to Ba or to Pb.

The equilibrium distribution coefficient D for (Ba, Ra) SO_4(s) is given by:

$$D = \frac{\dfrac{N_{RaSO_4(s)}}{N_{BaSO_4(s)}}}{\dfrac{(mRa^{2+})}{(mBa^{2+})}} \tag{4.4}$$

The Doerner-Hoskins (kinetic) coefficient, $\lambda$is given by

$$\lambda = \frac{\log \dfrac{(mRa_i{}^{2+})}{(mRa_f{}^{2+})}}{\log \dfrac{mBa_i{}^{2+}}{mBa_f{}^{2+}}} \tag{4.5}$$

Here, $N_{RaSO_4(s)}$ and $N_{BaSO_4(s)}$ are the molal fractions of Ra-226 and Ba in solid solution of the $BaSO_4$(s) crystal, (mRa^{2+}) and (mBa^{2+}) are the molal aqueous concentrations in solution, and the subscripts i and f refer to the initial and final solution concentrations.

In general form, the reaction of radium with any host crystal (MX) to form a mixed crystal (RaX) is written as:

$$Ra^{2+} + MX = M^{2+} + RaX \tag{4.6}$$

The value of D is given by

$$D = \frac{\dfrac{N_{RaX}}{N_{MX}}}{\dfrac{(mRa^{2+})}{(mM^{2+})}} \tag{4.7}$$

Here N_{RaX} and N_{MX} are, respectively, the molal fractions of radium and the parent cation in solid solution and (mRa^{2+}) and (mM^{2+}) are the molal aqueous concentrations of radium and of the parent metal cation in solution. The value of λ is given by:

$$\lambda = \frac{\log \dfrac{mRa_i^{2+}}{mRa_f^{2+}}}{\log \dfrac{mM_i^{2+}}{mM_f^{2+}}} \qquad (4.8)$$

Here, the subscripts "i" and "f" refer to the initial and final solution concentrations respectively of radium and the metal ion M.

At present, there is no apriori method to predict whether equilibrium (D) or kinetic (λ) conditions will be exhibited by the system. As noted in the appendix, one can direct the system towards a given distribution by the method used to force precipitation in the laboratory. Recently, thermodynamic data for predicting D have been developed. The data provide an estimate of equilibrium conditions and a reference point for viewing mill-formed coprecipitates.

4.2 Thermodynamics of Radium-226 in Metal Sulphates

A more fundamental way of describing the equilibrium equation

$$Ra^{2+} + MX = M^{2+} + RaX \qquad (4.9)$$

than using the distribution coefficient, D, is to relate it to thermodynamic quantities, and to account for ion activity coefficients, etc. For this reaction, the exchange coefficient K_{ex} is defined (Gordon et al, 1959; Langmuir and Riese, 1985) as:

$$K_{ex} = \frac{\gamma_{m^{2+}}\, mM^{2+}}{\gamma_{Ra^{2+}}\, mRa^{2+}} \quad \frac{\gamma_{RaX}\, N_{RaX}}{\gamma_{MX}\, N_{MX}} \qquad (4.10)$$

Here, γ and m are, respectively, the ion activity coefficients and molal concentration in aqueous solution while γ and N are respectively the rational activity coefficents and mole fractions in solid solution. The exchange coefficient is related to the Gibbs free energy of the reaction through the relationship

$$\Delta G^{o}_{ex} = RT \ln (K_{ex}) \tag{4.11}$$

and to other thermodynamic contants through the relationship

$$K_{ex} = K_{so}(MX)/K_{so}(RaX) \tag{4.12}$$

Here R is the universal gas constant
T is the absolute temperature
$K_{so}(MX)$ is the solubility product for pure crystalline MX
and $K_{so}(RaX)$ is the solubility product for pure crystalline RaX.

Inspection of the relationship for K_{ex} (Equation 4.10) and D (Equation 4.7); and the simplifications that in dilute solution, $\gamma_{M^{2+}} = \gamma_{Ra^{2+}}$, and that because RaX is a trace component in MX, $\gamma_{MX} \cong 1$ and $N_{MX} \sim 1$, lead to the relationship:

$$K_{ex} = \gamma_{RaX} D \tag{4.13}$$

For trace Ra in solid solution, one can use the relationship

$$N_{RaX} = D_{RaX} \frac{[Ra^{2+}]}{[M^{2+}]} \tag{4.14}$$

to estimate the equilibrium solid solution composition of radium in MX provided that the solution is saturated or supersaturated with respect to the host precipitate MX. The relationship (equation 4.14) assumes that the solution is sufficiently dilute that

$$mRa^{2+} = [Ra^{2+}]$$
and
$$mM^{2+} = [M^{2+}]$$

Values of the distribution coefficient D and of the rational activity coefficients derived by Langmuir and Riese (1985) are given in Table 4.1. D values for anhydrite are higher than these for gypsum ($CaSO_4.2H_2O$; Goldschmidt, 1944). Of note are the following points:

TABLE 4.1 DISTRIBUTION COEFFICIENTS (D) AND RATIONAL ACTIVITY (γ) COEFFICIENTS FOR TRACE RADIUM COPRECIPITATED IN VARIOUS METAL SULPHATES

Metal Sulphate	D (25°C)	D (100°C)	γ(25°C)	γ(100°C)
$CaSO_4$ (anhydrite)	(800) *	(40) *	(29.8) *	(5.6) *
$SrSO_4$ (celestite)	280	30	215	69.
$PbSO_4$ (angelsite)	11	3	26.8	8.4
$BaSO_4$ (barite)	1.8	0.90	1.11	0.75

* estimates

(i) Radium substitution in barium sulphate behaves almost as an ideal solution because the values for γ_{RaSO_4} in barite are near unity at 25°C.

(ii) At ambient radium concentration in natural waters (10^{-11} - 10^{-13} M), values of N_{RaX} are between 10^{-5} and 10^{-11}. These N_{RaX} values are sufficiently low that crystal strain caused by Ra substitution, in the parent lattice, is probably negligible (Langmuir and Riese, 1985). This means that one should be able to use simple thermodynamic principles to explain solid solution behaviour.

4.3 Metal Sulphates of Interest to this Investigation

Jarosite (e.g., $KFe_3(SO_4)_2(OH)_6.6H_2O$) and gypsum ($CaSO_4.2H_2O$) are the two metal sulphates which have been historically linked to radium behaviour in the uranium tailings because of Kaiman's (1977) observation of 80,000 pCi Ra-226/g jarosite (N_{RaX} = 2.1×10^{-7}) and 7,000 pCi Ra-226/g gypsum ($N_{RaX} = 3.8 \times 10^{-9}$). Barium sulphate is a controller of Ra-226 behavior in liquid effluents where sludges are formed by barium chloride addition to a solution containing a high concentration of sulpahte, but its potential importance in the leaching tanks and tailings was documented only recently (Constable and Snodgrass, 1983) in a study in which the potential control of lead sulphate was also examined.

Our recent literature review (see appendix) indicates that barium sulphate can be activated towards sorption of strontium and radium by heat treatment with calcium sulphate. This has suggested that a mixed solid solution of barium (calcium) sulphate would form which allows simultaneous or competititive coprecipitation of radium and strontium. Thus strontium needs to be considered as a potential controller of radium behaviour.

Accordingly, in this investigation, the theoretical and experimental data are used to evaluate the posssible coprecipitation of radium-226 with calcium, barium, lead, iron and strontium sulphates and the possible competition between strontium and radium, as coprecipitating cations within a mixed barium (calcium) sulphate. Due to the limits of the experimental time frame, the possibilities of formation of mixed crystals such as barium (calcium) sulphate, calcium (barium) sulphate, calcium (lead) sulphate, and calcium (strontium) sulphate and their role in capturing radium-226 as a coprecipitate remain unanswered.

5.0 PURPOSE AND DESIGN OF EXPERIMENTS

The model to be tested in this research is:

(i) that radium-226 dissolution behaviour in uranium tailings formed from sulphuric acid leaching is controlled by the dissolution of a parent crystal with which it is coprecipitated;

(ii) that this coprecipitate is formed in the first several leaching tanks;

(iii) that a coprecipitation mechanism rather than reversible adsorption in the leaching tanks controls the partitioning of Ra-226 onto the solid phase after dissolution of the parent U-238 mineral;

(iv) that the host crystal may be composed of sulphates of Ca, Ba, Sr, Fe and/or Pb.

(v) that this coprecipitate remains chemically stable in tailings piles until the porewater concentrations of sulphate are low enough to allow dissolution of the mixed crystal containing Ra-226;

To evaluate this model, several types of imformation are required:

(i) Identify the minerals from which radium, lead, barium, and other elements of concern are derived, using standard mineralogical and micro mineralogical techniques.

(ii) Identify the solids formed, the species in solution, their mineralogical sources, and the concentrations of each over time as the ore dissolves.

(iii) Identify the fate of each of these solids and species in the process stream.

(iv) Identify the surface precipitate (host crystal) containing Ra-226 and Ra-228 with direct observational techniques and identify the crystallization site.

(v) Evaluate and quantify the kinetics of dissolution of mono-minerals containing Ra-226, Ra-228, Ba, Pb, Ca, Fe and Sr.

(vi) Model these coprecipitation kinetics using data from simple laboratory systems to explain Ra-226/Ra-228 differences.

(vii) Evaluate steps (v) and (vi) in the heterogeneous mill system.

(viii) Couple steps (v), (vi) and (vii) with an evaluation of supersaturation conditions in the mill of the relevant parent crystal.

(ix) Validate that the same host solid controlling Ra-226 in the leaching pachua solids also controls its dissolution behaviour in old tailings.

(x) Trace the fate of each of the solids and soluble species in the mill processing streams from the time of placement of the tailings behind their containment structure, to the present.

To evaluate this model, experimentally, the following information is required:

(i) which cations, anions, and radionuclides are dissolved in the leaching tanks and how much of each;

(ii) which cations, anions, and radionuclides remain in solution in the leaching tanks;

(iii) what goes onto the solid phase after dissolution in the leaching tanks;

and (iv) which cations, anions and radionuclides are found on the surface of old tailings.

Three major types of experimental studies were conducted in order to obtain these data:

(i) acid digestion of raw ore;
(ii) washing experiments on various solids;
(iii) an adsorption experiment.

The objective of the experiments involving acid digestion of raw ore was to ascertain the quantities of different cations and Ra-226 which might be brought into solution and to determine which cations, etc., remained in sulphuric acid leaching solutions. This provides information about how much metal sulphate might form and data to evaluate the potential for formation of a mixed crystal containing Ra-226.

The objective of the washing experiments was to develop data which allows one to evaluate which cations, etc., can be dissolved and to see whether any one particular metal could explain Ra-226 dissolution behaviour. These experiments also provide insights to help explain the observations of others given in the literature.

The objective of the adsorption experiment was to ascertain whether adsorption could explain the solid solution distribution of radium-226 under the acidic conditions of the leaching pachucas.

For this study, the raw ore for the digestion experiments and the leaching pachuca solids were obtained from the Rio Algom Nordic mill. The tailings samples used were from the two main monitoring sites of the NUTP program - Gunnar (Northern Saskatchewan) and Lacnor (near Elliot Lake, above the Nordic Tailings Basin; cf Dubrowsky et al, 1985) and from the CCIW lysmeter used previously (Constable and Snodgrass, 1984).

6.0 ACID DIGESTION OF RAW ORE

Data in this chapter are used (i) to evaluate the supersaturation conditions in the leaching tanks so that potential host crystals may be identified, and (ii) to attempt to estimate how different acids affect mobilization of cations and radionuclides. The data are from laboratory digestion experiments and actual leaching conditions in a mill (Rio Algom, Nordic Mill) employing sulphuric acid leaching.

6.1 Laboratory Digestion Experiments

Methods

1 kg of raw feed solids was obtained from Rio Algom and kept covered with water until used. At the start of the experiment, the solids were washed with distilled water, air dried overnight and then divided into 50 gm lots. The solids were acid digested in **duplicate** under the conditions indicated in Table 6.1 at a S:L ratio of 1:3 (g/ml). The experiments at 25°C were mixed using a table shaker while those at 60°C were mixed using an air supply saturated with water. At the end of the digestion period, the solids were separated from the solution using a 0.45 µm filter, and the solutions were analyzed by DCP for cations, ion chromatography for anions and alpha, beta, or gamma spectrospy, for radionuclides. More details on the analytical procedures, laboratories used and the quality assurance program are given in the appendix.

Results and Discussion

The mean values of metal and radionuclide concentrations of the duplicates are given in Table 6.1. The data indicate that higher concentrations of aluminum, barium, potassium, and Ra-226 are observed in nitric acid and perchloric acid at 60°C then at 25°C whereas the concentrations of calcium, strontium, iron, lead, silica, uranium, and Th-230 are approximately independent of temperature. The activity of Pb-210 is also independent of temperature in perchloric acid solution. The concentrations of calcium, aluminum,barium, potassium, strontium, uranium, and Th-230 are similar in perchloric and nitric acid solutions, but the concentration of iron, lead, Pb-210 and Po-210 are higher in nitric acid then in perchloric acid solution. Because the ClO_4^- ion is more of an

TABLE 6.1 CONCENTRATIONS OF VARIOUS ELEMENTS IN LABORATORY DIGESTION EXPERIMENTS*

(Solids:Liquid Ratio = 1:3)

	3M	3M	3M	3M	3M	6M	6M
Digestion Acid	$HClO_4$	$HClO_4$	$HClO_4$	HNO_3	HNO_3	H_2SO_4	H_2SO_4
Digestion Time	3 hr	24 hr	24 hr	24 hr	24 hr	24 hr	24 hr
Digestion Temperature	25°C	25°C	60°C	25°C	60°C	25°C	60°C
	Concentration (mg/L) of Element						
Element							
SO_4	12,000	14,000	14,000	-	-	630,000	570,000
Ca	1,500	1,500	1,400	-	1,300	75	78
Al	143	210	620	-	480	150	700
Ba	0.8	0.8	4.4	0.8	3.7	LT 0.1	0.2
K	50	76	280	72	260	70	420
Sr	1.1	1.3	1.5	1.4	1.7	0.3	0.3
Fe	630	760	940	8,900	8,000	650	1,050
Pb	58	69	96	133	136	5.8	7.1
Si	89	83	84	130	160	4.7	6.6
U (Bq/L)	3,800	4,900	4,800	4,200	4,600	4,900	-
Th230 (Bq/L)	4,370	4,890	5,440	4,160	5,400	5,480	5,840
Ra226 (Bq/L)	426	386	883	155	640	65	41
Pb210 (Bq/L)	-	1,540	1,660	-	2,360	220	-
Po210 (Bq/L)	-	270	255	-	1,460	230	-
Th-232 (Bq/L)	1,000	870	933	620	1,500	1,200	1,284
Ra228 (Bq/L)	810	580	712	240	570	332	160
Th-228 (Bq/L)	1,260	1,200	1,250	1,100	1,700	1,360	1,300

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* Value given are mean of two duplicates.

indifferent anion than nitrate, it will form fewer inorganic complexes with cations than will nitrate. Thus, a plausible explanation of this trend is that larger concentrations of cations are expected in "nitrate" solutions than in chlorate solutions.

The respective activities of the U-238 and its decay series radionucides in **nitric** and **perchloric** acid solutions show that Th-230 activity mirrors that of uranium but that the solution activities of Ra-226, Pb-210 and Po-210 are substantially lower: Ra-226 is 10 to 20% of the expected value in nitric and perchloric acids, Pb-210 is 30 to 50% of the expected value and Pb-210 is 5% to 30% of the expected value. Because Th-230 activity is essentially the same as that of uranium, these data support the argument that the uranium mineral is dissolved by acid attack, liberating the daughters. They also show, however, that Ra-226, Pb-210 and Po-210 must be re-precipitated even in non-sulphate acid solutions. Because the equilibrium calculations (see next section) show that these solutions are supersaturated with respect to $BaSO_4$ and $PbSO_4$, it is probable that these three radionuclides have been re-precipitated as a metal sulphate of barium and or lead. The source of the sulphate in solution, while not explicitly clear, must be FeS and similar sulphide minerals that have dissolved and have been oxidized by dissolved oxygen in the strong acid solutions.

The activities of Th-232 and daughters in solution indicate that the solution activity of Th-228 is larger than that of its parents, although the difference between that of Th-232 and Th-228 is not large for most experimental solutions. Ra-228 levels range from 35% of Th-232 for nitric acid to 70 to 80% of Th-232 in the perchloric acid solution. Assuming similar chemical behaviour of Ra-226 and Ra-228 in the digesting solutions, one would expect a much lower Ra-228 activity in solution than observed.

The behaviour of several metals in the sulphuric acid solution is in sharp contrast to their behaviour in the nitric and perchloric acid solutions. The concentrations of calcium, barium, strontium, lead, silica, Ra-226 and Pb-210 are substantially lower in sulphuric acid solution. This can be explained by the formation of primary metal sulphate precipitates in sulphuric acid solution and coprecipitation of radiocations (Ra-226, Pb-210 and Po-210) in these metal sulphates. The concentrations of aluminum, potassium, uranium and thorium (230, 232, 228) in sulphuric acid solution are similar to those of the nitric and perchloric acid solutions while the behaviour of iron is similar to its behaviour in the perchloric acid solutions.

The activity of Ra-228 in sulphuric acid solution is approximately one-half of its activity in the nitric and perchloric acid solutions but it is substantially larger than that of Ra-226. This is additional evidence supporting the observation that the activity of Ra-226 in solution is much smaller than the activity of Ra-228 in solution.

6.2 Full Scale Digestion Experiment

Methods

This "experiment" involved obtaining leaching pachuca liquor samples from the Rio Algom leaching pachucas and measuring the concentrations of radionuclides, anions and cations in the liquor. The results are given in Table 6.2 for cations, and in Table 3.1 for radionuclides.

The samples for December 1984 were obtained from the leaching pachuca, but stood in the laboratory for two days to attain equilibrium, before the solids were separated from the solution using a glass fiber filter. The samples for the January 1985 and February 1985 sampling were obtained and filtered with a glass fiber filter within 1 hour of sampling. Visual inspection of the filtrate from the January 1985 sample after it had cooled (from 55°C to room temperature) and equilibriated for a week, showed the formation of a precipitate in the liquor. Accordingly in the February 1985 sampling, the leaching liquor samples were both allowed to equilibriate (the precipitate allowed to form) and diluted 1:10 immediately after filtration to prevent precipitation.

Results and Discussion

The results for the equilibriated conditions (with precipitate formation) from the February 1985 samples are given in Table 6.2 while those of the diluted liquor expressed as the original liquor concentrations are given as bracketed values. The composition of the solid is given in Table 6.3. The analytical results for the solution indicate that calcium is the only cation which is affected by the precipitation process while the solids data indicate that calcium and sulphate make up the largest portion of the solid. Hence, the precipitate formed after filtration and cooling is essentially a gypsum-type solid ($CaSO_4.2H_2O$) containing substantial-to-trace amounts of other cations such as aluminum, Th-230, and Ra-226. Application of these data to coprecipitation theory for

TABLE 6.2 CONCENTRATIONS OF VARIOUS ELEMENTS IN LEACHING PACHUCAS TANKS OF RIO ALGOM*

	Dec./84 Tank 12	Dec./84 Tank 12	Jan./85 Tank 1	Jan./85 Tank 12	Feb./85 Tank 1	Feb./85 Tank 3	Feb./85 Tank 5	Feb./85 Tank 7	Feb./85 Tank 11	Feb./85 Tank 12
Ca			700	610	790	680	700	680	730	780
(Ca)					(1,260)	(1,290)	(1,260)	(1,210)	(950)	(940)
Al			1,110	2,400	1,220	1,620	2,300	2,700	3,200	3,100
(Al)	-	-	-	-	(1,000)	(2,500)	(1,440)	(2,900)	(3,400)	(3,400)
Ba							0.1	0.2	0.3	0.3
(Ba)	-	-	-	-		(0.03)				
K			660	1,240	780	950	1,270	1,440	1,560	1,570
(K)	-	-	-	-	(610)	(1,380)	(840)	(1,570)	(1,820)	(1,770)
Sr			3.2	3.0	3.6	3.2	3.6	3.4	3.4	3.4
(Sr)	-	-	-	-	(3.7)	(3.8)	(3.6)	-	(3.5)	(2.9)
Fe			3,400	4,000	3,000	4,100	4,300	4,100	4,400	4,400
(Fe)	-	-	-	-	(3,600)	(4,600)	(3,600)	(4,500)	(4,600)	(4,500)
Pb			36	40	47	45	54	49	46	44
(Pb)	-	-	-	-	(45)	(49)	(48)	(48)	(41)	(41)
Si			1,080	1,200	1,020	1,020	1,110	1,120	1,290	890
(Si)	-	-	-	-	(940)	(1,000)	(920)	(1,000)	(1,040)	(810)

* Bracketted quantities indicate concentration of a 1:10 dilution of parent liquor to prevent gypsum precipitation expressed as the original liquor concentration.

TABLE 6.3 CONCENTRATION OF CATIONS AND ANIONS IN GYPSUM PRECIPITATE*

Element	Mean Concentration	Std. Dev.	Number of Samples
Ca	183 mg/g	39 mg/g	8
SO_4	625 mg/g	32 mg/g	8
Ba	16 ug/g	12 ug/g	8
Sr	163 ug/g	36 ug/g	8
Fe	16 mg/g	6 mg/g	8
Pb	559 ug/g	270 ug/g	8
Ra-226	3.0 Bq/g	3.2	8

* Other metals present: Be, Mo, V, Al, Mg, K, Na, Zn, Cd, Mn, Co, Ca, Cr, Ni, Si, U, Th

* Other radionuclides present: Th-230, 232, 228, Ra-228, Pb-210, Po-210

solids such as gypsum will await future work, although it presents the basis for modelling certain aspects of tailings behaviour connected with gypsum dissolution and formation.

The molar ratio of $Ca:SO_4$ in the solid precipitated in the filtered leaching liquor is 1:1.4. An empirical, electroneutral formulae for this solid, $CaSO_4\,(H_2SO_4)_{0.4}$, indicates an enrichment of the solid with sulphate ion. This could result from imperfect gypsum formation and the fact that part of the precipitate had a "gelatinous" nature after the liquor was decanted from the solid and the solid washed with distilled water. The total mass given in Table 5.4 is less than 1 g, the unit weight of the solids. But if the calcium is assumed to represent gypsum with a formula of $CaSO_4.2H_2O$, the waters of hydration (165 mg/g) together with other metals (Al, Fe, U etc) give a mass balance (i.e., 1g/g).

Of interest also is how well the laboratory experiments emulate the leaching pachucas system. The best comparison is between the sulphuric acid experiments (Table 6.1) and the leaching liquor observations (Table 6.2; Table 3.1). Upon first inspection, the cation and radionuclide concentrations in the laboratory experiment at 60°C (Table 6.1) would appear to be low despite the use of 6 M sulphuric acid in the laboratory experiment (the leaching tank of sulphate concentration is approximately 1 M). However, the laboratory experiment was conducted at a 1:3, S:L ratio while the leaching tank S:L ratio is approximately 1:1. When account is taken of these differences, then the mass of elements such as Al, K, Fe and Th-230 dissolved in the laboratory experiment are close to those of the leaching pachucas. The major differences for metals such as calcium, strontium, lead, and barium are explained by the role of precipitation of their metal sulphate. The main remaining differences are the higher concentrations of uranium and silica observed in the leaching pachucas compared to those of the laboratory experiments.

6.3 Analysis of Acid Digestion Data

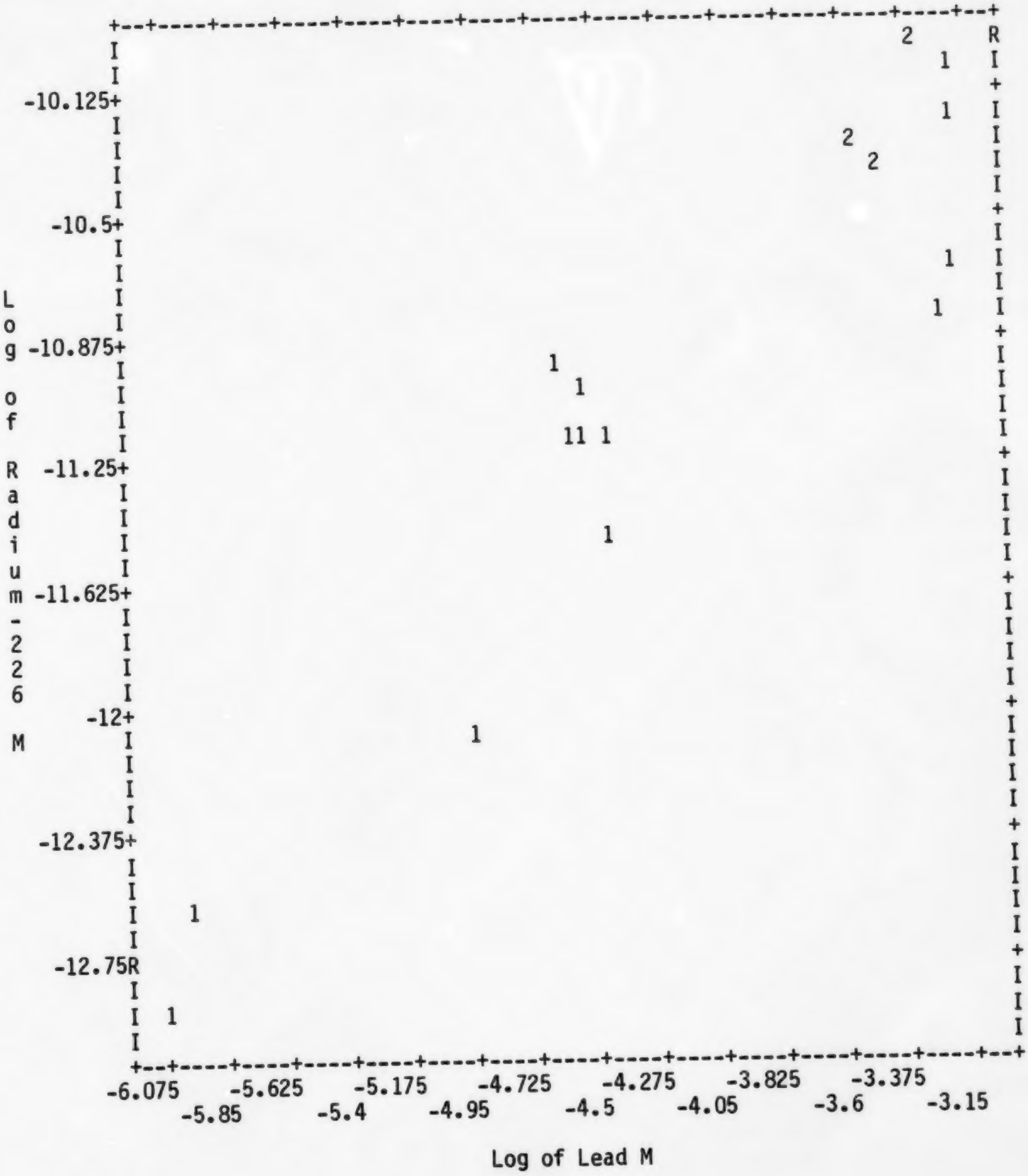
Relationships of Ra-226 and Cations

A correlation analysis of Ra-226 with various cations (Ca, Ba, Sr,Fe, Pb) and of the cations with themselves was made for these experiments. Plots of concentration (M) of Ra-226 with concentration (M) of Ba and Pb are given here (Fig. 6.1(a) and (b) for the laboratory digestion; Fig. 6.2(a) and (b) for the leaching pachucas). Other plots are given

6.1(a) Correlation of Ra with Ba in Acid Digestion Experiment

```
         +----+----+----+----+----+----+----+----+----+----+----+----+----+---R+----++
         I                                                                 2    I
         I                                                               1      I
  -10.125+                                                                      +
         I                                                               1      I
         I                                            1 1                       I
         I                                            2                         I
         I                                                                      I
    -10.5+                                                                      +
         I                                                                      I
         I                                            1                         I
L        I                                                                      I
o        I                                         1                            I
g -10.875+                                                                      +
         I                                           1                          I
o        I                1                                                     I
f        I                                                                      I
         I    1                      1         1                                I
R  -11.25+                                                                      +
a        I                                                                      I
d        I                                                                      I
i        I                           1                                          I
u        I                                                                      I
m -11.625+                                                                      +
-        I                                                                      I
2        I                                                                      I
2        I                                                                      I
6        I                                                                      I
      -12+                                                                      +
M        I       1                                                              I
         I                                                                      I
         R                                                                      I
         I                                                                      I
  -12.375+                                                                      +
         I                                                                      I
         I                                                                      I
         I    1                                                                 I
         I                                                                      I
   -12.75+                                                                      +
         I                                                                      I
         I       1                                                              I
         I                                                                      I
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----+----++
              -6.475    -6.125    -5.775    -5.425    -5.075    -4.725    -4.375
          -6.65      -6.3     -5.95      -5.6     -5.25      -4.9     -4.55

                                     Log of Barium M

19 cases plotted. Regression statistics of RA on BA:
Correlation  .87533 R Squared  .76620  S.E. of Est     .42585 Sig.  .0000
Intercept(S.E.)   -5.30930(   .75769)  Slope(S.E.)     1.01699(   .13625)
```

6.1(b) Correlation of Ra with Pb in acid Digestion Experiment

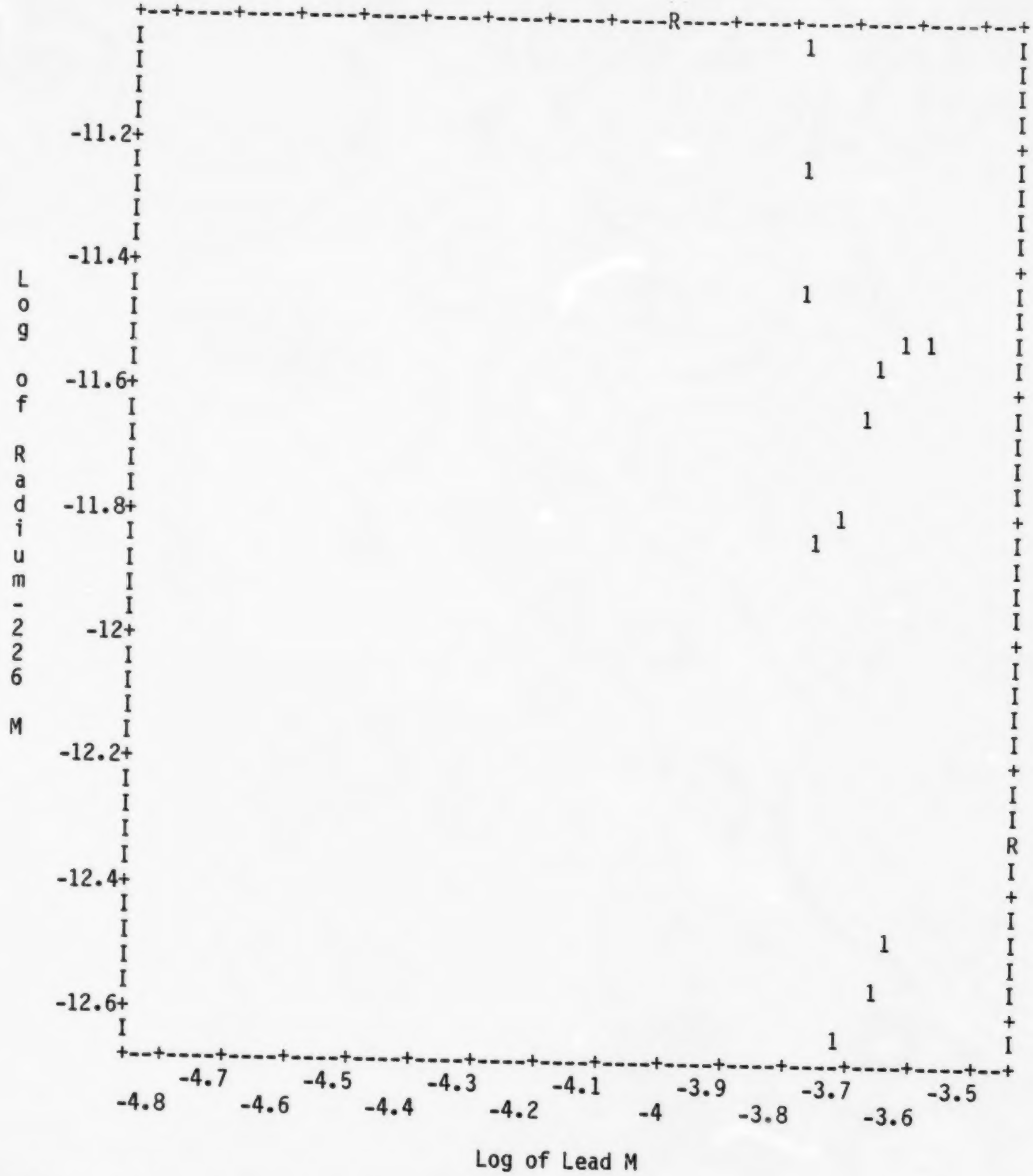


```
19 cases plotted. Regression statistics of RA on PB:
Correlation  .94015 R Squared  .88388  S.E. of Est     .30011 Sig.  .0000
Intercept(S.E.)   -7.32806(   .32296)  Slope(S.E.)     .87703(    .07710)
```

6.2(a) Correlation of Ra with Ba in Leaching Pachucas Liquor

```
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
         I                                                      1               I
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.2+                                                                      +
         I                                                                1     R
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.4+                                                                      +
L        I                                                      1               I
o        I                                                                      I
g        I                                      1         1                     I
         I                                                      1               I
o   -11.6+                                                                      +
f        I                                                      1               I
         I                                                                      I
R        I                                                                      I
a        I                                                                      I
d   -11.8+               1                                                      +
i        I     1                                                                I
u        I                                                                      I
m        I                                                                      I
-        I                                                                      I
2     -12+                                                                      +
2        I                                                                      I
6        I                                                                      I
         I                                                                      I
M        I                                                                      I
    -12.2+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         R                                                                      I
    -12.4+                                                                      +
         I                                                                      I
         I    1                                                                 I
         I                                                                      I
         I    1                                                                 I
    -12.6+                                                                      +
         I                                     1                                I
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
             -7.05     -6.75     -6.45     -6.15     -5.85     -5.55     -5.25
         -7.2      -6.9      -6.6      -6.3        -6      -5.7      -5.4

                                    Log of Barium M

12 cases plotted. Regression statistics of RA on BA:
Correlation  .71132 R Squared  .50597  S.E. of Est    .38322 Sig.  .0095
Intercept(S.E.)   -8.38562( 1.06280)  Slope(S.E.)     .54557(  .17048)
```

6.2(b) Correlation of Ra with Pb in Leaching Pachucas Liquor



```
12 cases plotted. Regression statistics of RA on PB:
Correlation -.29663 R Squared  .08799  S.E. of Est    .52068 Sig.  .3491
Intercept(S.E.)  -20.41450(  8.80359) Slope(S.E.)   -2.33875(  2.38101)
```

in the appendix. Generally the plots and the correlation coefficients indicate that radium is correlated only with barium and lead concentration in the digestion solutions while correlations of radium-226 with Ca, Sr and Fe are quite scattered. Correlation plots of the individual metals with each other show some degree of relationship although they are not very strong.

These plots suggest that, in addition to the barium hypothesis (Constable and Snodgrass, 1983), lead in a lead sulphate may also influence Ra-226 behaviour in leaching systems. A summary of the correlation statistics is given in Table 6.4.

Speciation/Equilibrium Calculations

The anion-cation data for the laboratory experiment and leaching tank data (diluted concentration data for calcium from Table 6.2) were evaluated using an equilibrium chemistry computer code (REDEQL; Morel and Morgan, 1972) capable of evaluating speciation and precipitation. The significant thermodynamic constants of interest to this project are given in Table 6.5 and the solids predicted to precipitate are given in Table 6.6. The possible formation of jarosite was not evaluated in the calculations.

The amount of solid phase predicted to precipitate is considered by this author to be approximate rather than exact because the ion activity corrections are imprecise in solutions having an ionic strength greater than 0.5 M. For such solutions, the ion interaction model of Pitzer is required to evaluate ion activity coefficients more precisely. In the calculations given in this report, an ionic strength of 0.5 M is imposed, this being the upper limit of the range of validity for the extended Debeye-Huckel equation (Stumm and Morgan, 1981).

The calculations suggest that barium sulphate, lead sulphate, and amorphorus silica should precipitate in the laboratory experiments and that barium sulphate, gypsum, lead sulphate and amorphorus silica should precipitate in the leaching pachuca liquor. The laboratory solutions are close to saturation with respect to calcium sulphate, but far from saturated conditions with respect to strontium sulphate.

TABLE 6.4 CORRELATION COEFFICIENT AND SLOPE OF RELATIONSHIP BETWEEN Ra-226 AND BARIUM AND Ra-226 AND LEAD

	Ra^{226} - Ba		Ra^{226} - Pb	
Experiment	r^2	Slope	r^2	Slope
Acid Digestion (Fig. 6.1)	.766	1.02	.884	0.877
Leaching Pachucas (Fig. 6.2)	.506	0.546	.088	-.30
EDTA on LP Solids (Fig. 7.1)	.947	0.918	.764	1.48
EDTA Kinetic Experiment	.116	0.370	.941	1.08
EDTA on Well Washed Solids (Fig. 7.2)	.925	0.927	.593	0.936
Salt wash of LP Solids (Fig. 7.3)	.910	0.888	.629	0.986
Ca/Ba wash of LP Solids (Fig. 7.4)	-	-	.909	1.33
Acid wash of LP Solids (Fig. 7.5)	.974	.951	.883	1.55
EDTA on Gunnar Tailings (Fig. 7.6)	.983	.883	.140	0.444
EDTA on Lac Nor Tailings (Fig. 7.7)	.892	.710	.354	0.762
EDTA on Misc. Tailings	.878	.645	.701	1.13
Acid Digestion Solids (Fig. 7.8)	.734	.929	.326	0.654
EDTA on LP Solids (Fig. 9.1)	.868	.946	.672	1.06
Salts and Acids of LP Solids (Fig. 9.3)	.944	.954	.779	1.30
All Tailings Solids (Fig. 9.4)	.775	.734	.390	.679
All Data (Fig. 9.5)	.838	.859	.452	.748

TABLE 6.5

THERMODYNAMIC CONSTANTS USED IN EQUILIBRIUM CALCULATIONS

Cation/Anion	Complexation Constant (pK)	Solubility Constant (pK_{so})
$BaSO_4$	2.7 (3)	9.97 (4)
$PbSO_4$	2.7 (1)	7.7 (1)
$SrSO_4$	2.55 (3)	6.64 (4)
$RaSO_4$	2.76 (2)	10.26 (5)
$CaSO_4$	2.3 (1)	4.7 (1)
		4.61 (6)

Source

(1) Morel and Morgan (1972)
(2) Smith and Martell
(3) Benes (1982)
(4) Langmuir and Riese (1985)
(5) Nikitin and Tolmatschefl (1933)
(6) Christopherson and Christopherson (1976)

TABLE 6.6

SOLIDS CALCULATED TO FORM IN ACID DIGESTION SOLUTIONS

6.6 a Solids Calculated for Laboratory Digestion Experiment

% of Metal as $MeSO_4$ Precipitated in Solution Number:

Solid	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15*
$CaSO_4$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$BaSO_4$	89	90	95	95	97	99	96	95	99	98	87	66	95	95	0
$SrSO_4$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$PbSO_4$	54	55	77	79	82	84	69	91	90	88	56	56	63	64	0

* Distilled Water (Control)

6.6 b Solids Calculated for Leaching Pachucas Liquor

% of Metal as $MeSO_4$ Precipitated in Solution Number:

Solid	1	2	3	4	5	6	7	8
$CaSO_4$	44	8	59	59	57	49	36	35
$BaSO_4$	45	33	36	35	87	93	95	95
$SrSO_4$	0	0	0	0	0	0	0	0
$PbSO_4$	92	91	93	92	94	92	92	92

The amount of gypsum predicted to precipitate in the leaching pachuca liquor (Table 6.6b) corresponds approximately to the amount observed to precipitate (see Table 6.2); this provides some verification for the thermodynamic constants (Table 6.5) used for gypsum.

Why the solution is super-saturated with respect to lead sulphate and barium sulphate is unclear, particularly because the samples were allowed to equilibriate for 1-4 weeks. In the same sample bottle containing leaching liquor, a gypsum solid formed, but the solution remained supersaturated with respect to barite and anglesite. The precipitation kinetics of barium sulphate at this degree of super-saturation should be sufficiently rapid to allow precipitation. It is plausible that much of the barium and lead is present as small sols of diameter 100-200A^{o} or that the thermodynamic data are erroneous in concentrated sulphuric/nitric/perchloric acid solutions. The former (sol) is the most plausible explanation.

6.4 Summary of Digestion Experiments

The equilibrium calculations indicate that radium-226 coprecipitation with lead sulphate and barium sulphate is possible because the solutions are super-saturated with respect to these solids. The coprecipitation with gypsum is also possible, because the solutions are either supersaturated or near to equilibrium with respect to gypsum.

The correlations of Ra-226 with various metals (Ca, Ba, Sr, Pb, Fe) in solution indicate that only barium and lead consistently show a correlation with Ra-226 in solution. This suggests that Ra-226 coprecipitation with sulphates of calcium (gypsum), strontium (celesite) and iron (e.g., jarosite) is not significant.

The laboratory experiments reasonably emulate leaching pachuca processes when aluminum, potassium and Th-230 are used as marker elements for comparison purposes to data for sulphuric acid solutions. When perchloric and nitric acid solution data are compared to leaching pachuca data, approximately 3 times more Ca, 10-40 times more barium, and 8-10 times more lead are brought into solution than suggested by leaching tank data. But the amount of strontium digested in the laboratory experiments is approximately the same as that measured in the leaching pachuca liquor. The excess of calcium, barium, and lead must be re-precipitated in the leaching pachucas as a metal sulphate while strontium remains under-saturated with respect to its metal sulphate.

There are two possible explanations for the Ra-226/Ra-228 differences: (i) the origin of the metal ion involved in the formation of a parent sulphate is physically located much closer to Ra-226 than to Ra-228 in the ore; and (ii) dissolution kinetics of minerals containing barium and lead. A plausible explanation is that the (Me, Ra-226)SO_4 mixed crystal is formed near to the mineral containing Ra-226 and further from the mineral containing Ra-228. Stable lead (Pb-206) is found in the uranium mineral, because it is the stable end-product of the U-238 chain. Barium may also be present in or near to the uranium mineral. Stable lead Pb-208 is also found in significant amounts in monazite (the typical mineral containing Th-232). Less Ra-228 would be coprecipitated relative to the amount of Ra-226 coprecipitated if the nucleation site for the parent metal sulphate is the uranium mineral or an auxiliary mineral cemented to the uranium mineral.

If dissolution kinetics control the Ra-226/Ra-228 differences, the following processes may explain the phenomena. Leaching of uranium minerals (e.g., uraninite) appears to be much faster than leaching of thorium (-232) minerals (e.g., monazite). If barium-containing minerals also dissolve quickly, U, Ra-226, Pb-210, Pb-206 (stable), and Ba will be in solution before much Th-232, Ra-228, and Th-228 is dissolved. Provided the leaching solution is supersatured with respect to barium sulphate and lead sulphate, their precipitation and incorporation of Ra-226 will remove Ra-226 from solution. If most of radium is coprecipitated by $BaSO_4(s)$, (as opposed to by $PbSO_4(s)$), and if precipitation of most of barium occurs before much Ra-228 dissolves, the coprecipitation kinetics of Ra-228 will be slow. Hence, after 24-36 hr of leaching, most of the Ra-226 will be reprecipitated, but a much smaller fraction of Ra-228 will be reprecipitated.

7.0 WASHING EXPERIMENTS ON VARIOUS SOLIDS

Experiments in this chapter are designed to evaluate which cations and radionuclides go onto the LP solids in the leaching tanks and to determine relationships between Ra-226 and cations in dissolution experiments. These data give evidence concerning which crystal may control the dissolution of Ra-226 and data for comparison with the thermodynamics of coprecipitation.

The following experiments were carried out with various washing agents:

(i) EDTA on Leaching Pachuca Solids
(ii) EDTA on Well-Washed Leaching Pachuca Solids
(iii) EDTA Kinetic Experiment on Leaching Pachuca Solids
(iv) Chloride Salts and Acid Washing of Leaching Pachuca Solids
(v) EDTA, H_2SO_4, and KCl on Gunnar Solids
(vi) EDTA, H_2SO_4, and KCl on Lacnor Solids
(vii) EDTA on various other tailings samples.

7.1 EDTA Extraction of Leaching Pachuca (LP) Solids

Methods

Leaching pachuca solids were obtained from Tank #12 of Rio Algom, (Quirke Mill, December, 1984) and allowed to equilibriate in the laboratory two days. The leaching liquor data are given in Table 6.2. The solids were separated by filtration, washed twice with dilute sulphuric acid and allowed to air dry overnight. The residual moisture was approximately 10%.

The solids were divided into 50 gm lots and contacted with various EDTA solutions (10^{-5} M to 1 M) and a control (distilled water) for one hour at 25°C generally at a S:L ratio of 1:3 (see Table 7.1) using magnetic stirrers. The solids were separated from solution by filtration (glass fiber filter followed by 0.45 μm filter). Cations were analyzed byDCP instrumentation, anions (sulphate, chloride, fluoride) by ion chromatography, pH by pH meter, and inorganic carbon by Beckman CO_2 analyzer.

TABLE 7.1 ANALYTICAL RESULTS FROM EDTA EXPERIMENT ON LEACHING PACHUCA SOLIDS

			Concentrations*							
Experimental Condition	S:L	pH	SO_4^{2-}	Ca	Al	Ba	Sr	Fe	Pb	Ra226 Bq/L
10^{-5} M EDTA	1:3	10	980	115	0.2	0.10	0.21	-	9.0	7.0
10^{-4} M EDTA	1:3	10	1,160	111	0.19	0.12	0.22	0.24	15	8.8
10^{-4} M EDTA	1:3	10	1,090	102	0.18	0.10	0.29	0.08	14.9	8.0
10^{-3} M EDTA	1:3	10	1,240	139	0.25	0.04	0.21	11.5	32	8.8
10^{-2} M EDTA	1:3	10	-	124	1.30	1.16	0.59	28	48	330
10^{-2} M EDTA	1:3	10	760	269	0.46	4.5	1.10	31	54	550
10^{-1} M EDTA	1:3	10	1,150	151	0.82	-	-	61	89	1,662
10^{-1} M EDTA	1:3	10	1,050	304	0.49	10.2	1.13	66	90	1,808
10^{-1} M EDTA	1:3	10	1,090	301	0.58	16.0	1.14	62	91	1,710
1 M EDTA	1:3	10	1,260	246	0.57	14.3	0.91	54	120	1,989
Distilled	1:3	10	1,150	118	0.18	0.15	0.18	4.7	9.2	16.5
10^{-1} M EDTA	1:1	10	3,600	530	3.3	32	2.2	188	270	3,987
10^{-1} M EDTA	1:8	10	590	89	0.9	7	0.4	33	52	774
10^{-1} M EDTA	1:3	7	1,500	210	20	12.3	0.9	82	100	1,417
10^{-1} M EDTA	1:3	12	1,400	220	3	16	10	74	94	1,764

* Units: mg/L except for pH and Ra-226

Results and Discussion

Results for representative cations and sulphate are given in Table 7.1. The reproducability between duplicate treatments is quite good (generally within 10%, see Table 7.1). The analytical reproducibility (repeat chemical analysis of the same sample; not shown) is of the order of 5%.

The results (Table 7.1) show that higher concentrations of the cations are brought into solution with higher concentrations of EDTA, and with lower liquid-to-solid ratios. The cation concentration is approximately independent of pH in the range of 7-12. The standard condition of pH=10 was chosen because the work of Nixon et al (1982) demonstrates that this is an optimum pH with EDTA extraction.

The concentration of cations extracted in 1 M EDTA solution concentration is approximately the same as for 0.1 M EDTA solutions. This is unexpected but is explainable by complexation considerations. The data of Table 7.1 and that of the other cations and anions not given in Table 7.1 were analyzed with REDEQL (Morel and Morgan, 1972), considering all possible cation-anion complexes. The calculations indicate that at 0.1 M EDTA, some of the EDTA is free (i.e., available to complex metals) whereas at 1 M EDTA, much of the EDTA is complexed with sodium. This results from substantially larger quantities of sodium added as NaOH to the 1 M EDTA solution than to the 0.1 M EDTA solution to maintain a pH of 10.

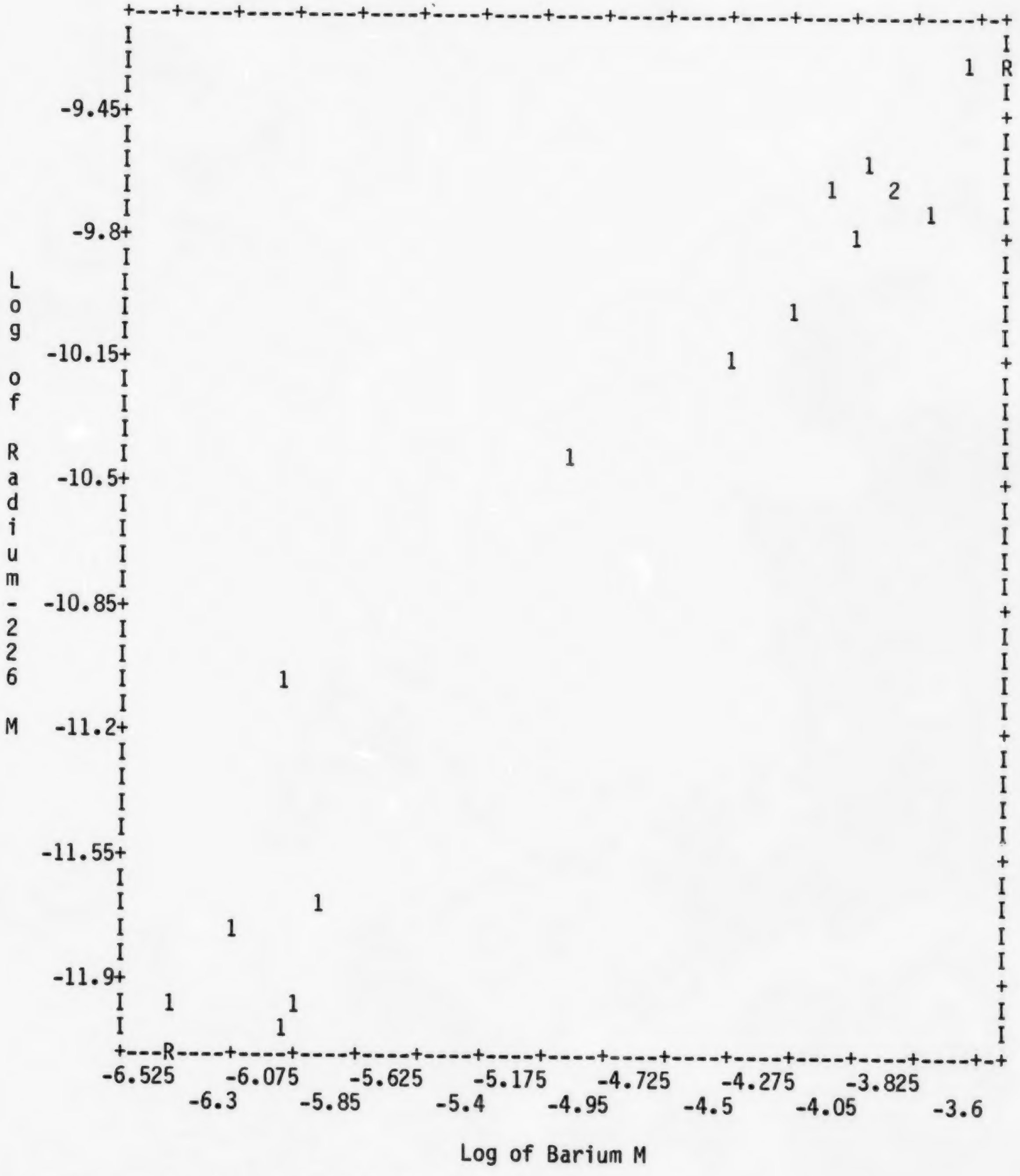
The radium concentrations are plotted against Ca, Ba, Sr, Fe, and Pb in Fig. 7.1(a) to (e). Overall the data show a generally positive relationship between the concentration of Ra-226 and the cations; this results from the increasing concentration of metals extracted as a function of EDTA concentration. But, by inspection of Fig. 7.1 (a) to (e), the Ra-226 relationships with Ca, Sr, and Fe are much more noisy than the relationships with Ba and Pb. This is confirmed by their respective correlation coefficients (see also Table 6.4). This suggests that metal sulphates of barium or lead are plausible candidates to explain Ra-226 behaviour.

Inspection of the Ra-Ca plot (Fig. 7.1a) suggests two populations of data - one at low calcium concentrations and one at high calcium concentrations. This would be explained by mill-formed gypsum co-deposited with a (Ba, Ra)SO_4 or (Pb, Ra)SO_4 (high calcium

7.1(a) Correlation of Ra with Ca in EDTA-LP Solids Experiment

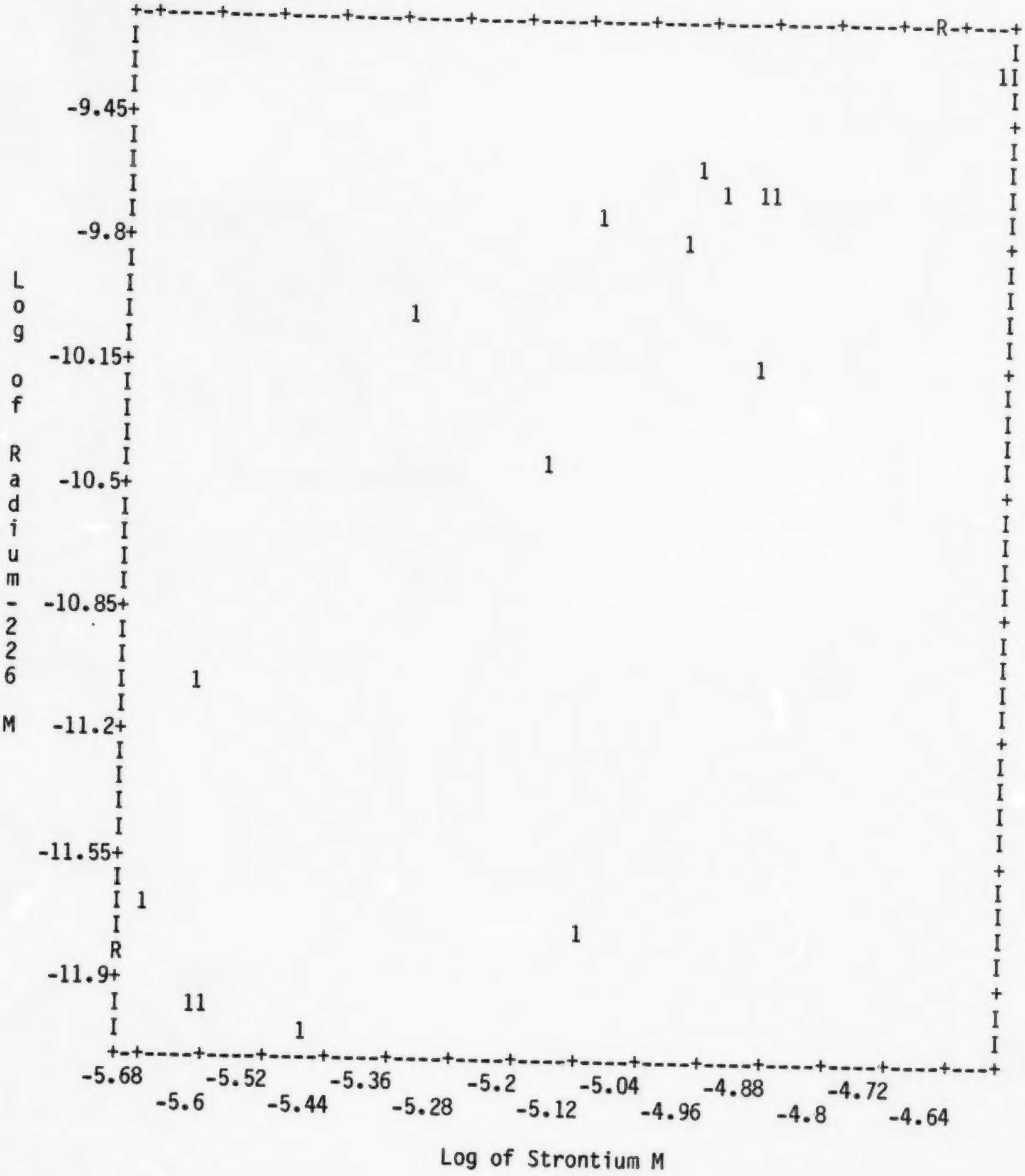
```
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
          I                                                                      I
          I                                                                  1   I
          I                                                                      I
     -9.45+                                                                      +
          I                                                                      I
          I                                        1                             I
          I                                    1          2                      R
          I                                  1                                   I
      -9.8+                                  1                                   +
          I                                                                      I
 L        I                                                                      I
 o        I   1                                                                  I
 g        I                                                                      I
    -10.15+                                           1                          +
 o        I                                                                      I
 f        I                                                                      I
          I                                                                      I
 R        I               1                                                      I
 a   -10.5+                                                                      +
 d        I                                                                      I
 i        I                                                                      I
 u        I                                                                      I
 m        I                                                                      I
 -  -10.85+                                                                      +
 2        I                                                                      I
 2        I                                                                      I
 6        I            1                                                         I
          I                                                                      I
 M   -11.2+                                                                      +
          R                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
    -11.55+                                                                      +
          I                                                                      I
          I             1                                                        I
          I                                                                  1   I
          I                                                                      I
     -11.9+                                                                      +
          I           1       1                                                  I
          I        1                                                             I
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
                -2.58     -2.46     -2.34     -2.22      -2.1     -1.98     -1.86
           -2.64     -2.52      -2.4     -2.28     -2.16     -2.04     -1.92

                                     Log of Calcium M

16 cases plotted. Regression statistics of RA on CA:
Correlation  .46586 R Squared  .21703  S.E. of Est     .93774 Sig.  .0690
Intercept(S.E.)   -5.94696( 2.34115)  Slope(S.E.)    1.97928( 1.00475)
```

7.1(b) Correlation of Ra with Ba in EDTA-LP Solids Experiment



```
16 cases plotted. Regression statistics of RA on BA:
Correlation  .97316 R Squared  .94704  S.E. of Est    .24389 Sig.  .0000
Intercept(S.E.)   -6.03379(   .29099)  Slope(S.E.)     .91821(   .05803)
```

7.1(c) Correlation of Ra with Sr in EDTA-LP Solids Experiment



```
16 cases plotted. Regression statistics of RA on SR:
Correlation  .83430 R Squared  .69605  S.E. of Est     .58426 Sig.  .0001
Intercept(S.E.)    2.75879(  2.35246)  Slope(S.E.)    2.56522(   .45304)
```

7.1(d) Correlation of Ra with Fe in EDTA-LP Solids Experiment

```
       ++----+----+----+----+----+----+----+----+----+----+----+----+----+----+
        I                                                                      I
        I                                                          1           I
        I                                                                      I
   -9.45+                                                                      +
        I                                                                      R
        I                                                 1                    I
        I                                                  21                  I
        I                                                  1                   I
    -9.8+                                                    1                 +
        I                                                                      I
L       I                                                                      I
o       I                                             1                        I
g       I                                                                      I
  -10.15+                                             1                        +
o       I                                                                      I
f       I                                                                      I
        I                                                                      I
R       I                                            1                         I
a  -10.5+                                                                      +
d       I                                                                      I
i       I                                                                      I
u       I                                                                      I
m       I                                                                      I
- -10.85+                                                                      +
2       I                                                                      I
2       I                                                                      I
6       I                       1                                              I
        I                                                                      I
M  -11.2+                                                                      +
        I                                                                      I
        I                                                                      I
        I                                                                      I
        I                                                                      I
  -11.55+                                                                      +
        I                                                                      I
        I            1                                                         I
        I                                                                   1  I
        I                                                                      I
   -11.9+                                                                      +
        I           1                           1                              I
        I   1                                                                  I
        +R----+----+----+----+----+----+----+----+----+----+----+----+----+----+
           -5.7      -5.1      -4.5      -3.9      -3.3      -2.7      -2.1
        -6      -5.4      -4.8      -4.2      -3.6        -3      -2.4

                                  Log of Iron M

16 cases plotted. Regression statistics of RA on FE:
Correlation   .67496 R Squared   .45557  S.E. of Est     .78195 Sig.  .0041
Intercept(S.E.)   -8.36267(   .66428) Slope(S.E.)      .61430(   .17948)
```

7.1(e) Correlation of Ra with Pb in EDTA-LP Solids Experiment

```
         +----+----+----+----+----+----+----+----+----+----+----+----+----+--R-++
         I                                                                      I
         I                                                                   1  I
         I                                                                      I
    -9.45+                                                                      +
         I                                                                      I
         I                                                         1            I
         I                                                     3                I
         I                                                     1                I
     -9.8+                                                      1               +
         I                                                                      I
L        I                                                                      I
o        I                                              1                       I
g        I                                                                      I
   -10.15+                                               1                      +
o        I                                                                      I
f        I                                                                      I
         I                                                                      I
R        I                                             1                        I
a   -10.5+                                                                      +
d        I                                                                      I
i        I                                                                      I
u        I                                                                      I
m        I                                                                      I
-  -10.85+                                                                      +
2        I                                                                      I
2        I                                                                      I
6        I                        1                                             I
         I                                                                      I
M   -11.2+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
   -11.55+                                                                      +
         I                                                                      I
         I                1                                                     I
         I                         1                                            I
         I                                                                      I
    -11.9+                                                                      +
         I  1                                     1                             I
         I                               1                                      I
         +----+----+---R+----+----+----+----+----+----+----+----+----+----+----++
        -5.075    -4.725    -4.375    -4.025    -3.675    -3.325    -2.975
               -4.9    -4.55       -4.2     -3.85      -3.5     -3.15      -2.8

                                     Log of Lead M

16 cases plotted. Regression statistics of RA on PB:
Correlation  .87397 R Squared  .76382  S.E. of Est     .51503 Sig.  .0000
Intercept(S.E.)   -4.98556(   .83481) Slope(S.E.)    1.47664(   .21945)
```

TABLE 7.2

RADIUM ACTIVITY IN WASHING WATERS USING SALTS AND ACIDS

a) Radium Activity (Bq/L) for S:L = 1.3; 1 hr leaching

Strength of Agent

0.0001 M		0.001 M		0.01 M		0.1 M		1 M	
Agent	Activity	Agent	Activity	Agent	Activity	Agent	Activity	Agent	Activity
$CaCl_2$	45.6	$CaCl_2$	78	$CaCl_2$	84	KCl	243	KCl	1,690
	72.7		90	HCl	42		279		1,708
		$BaCl_2$	225		41	$FeCl_3$	1,625	$FeCl_3$	1,807
			259	$BaCl_2$	924				2,071
					849			$CaCl_2$	1,616
									1,362
									1,464
									1,504
								HCl	1,985
									1,854
								$HClO_4$	1,968
									2,207
								HNO_3	1,921
									1,357
								H_2SO_4	11.3
									3.4

b) Radium Activity (Bq/L) for S:L = 1:20, 1 hr leaching

Strength of Agent

0.1 M		1 M	
Agent	Activity	Agent	Activity
KCl	393	KCl	339
	414		480
$FeCl_3$	475	$FeCl_3$	343
			362
			(5 min.)
$CaCl_2$	234	$CaCl_2$	483
			288
			(5 min.)

concentrations) and a gypsum formed during the slower equilibration process (low calcium concentrations). This possibility was investigated by obtaining new samples and using a more carefully controlled sample preparation technique. The experiment and results are described next.

7.2 EDTA Extraction of Well-Washed Leaching Pachuca Solids (Exp.12A)

Methods

Leaching pachucas solids, obtained from LP#12 of the Rio Algom Quirke Mine in February 1985 were immediately filtered and then washed twice with dilute sulphuric acid. They were then washed with distilled water until the pH of the distilled water filtrate was greater than 4 and the resultant calcium concentration was less than 10^{-5} M. The cation-anion data of this leaching pachuca liquor (of T12) are given in Table 6.2 and the radionuclide data are given in Table 3.1.

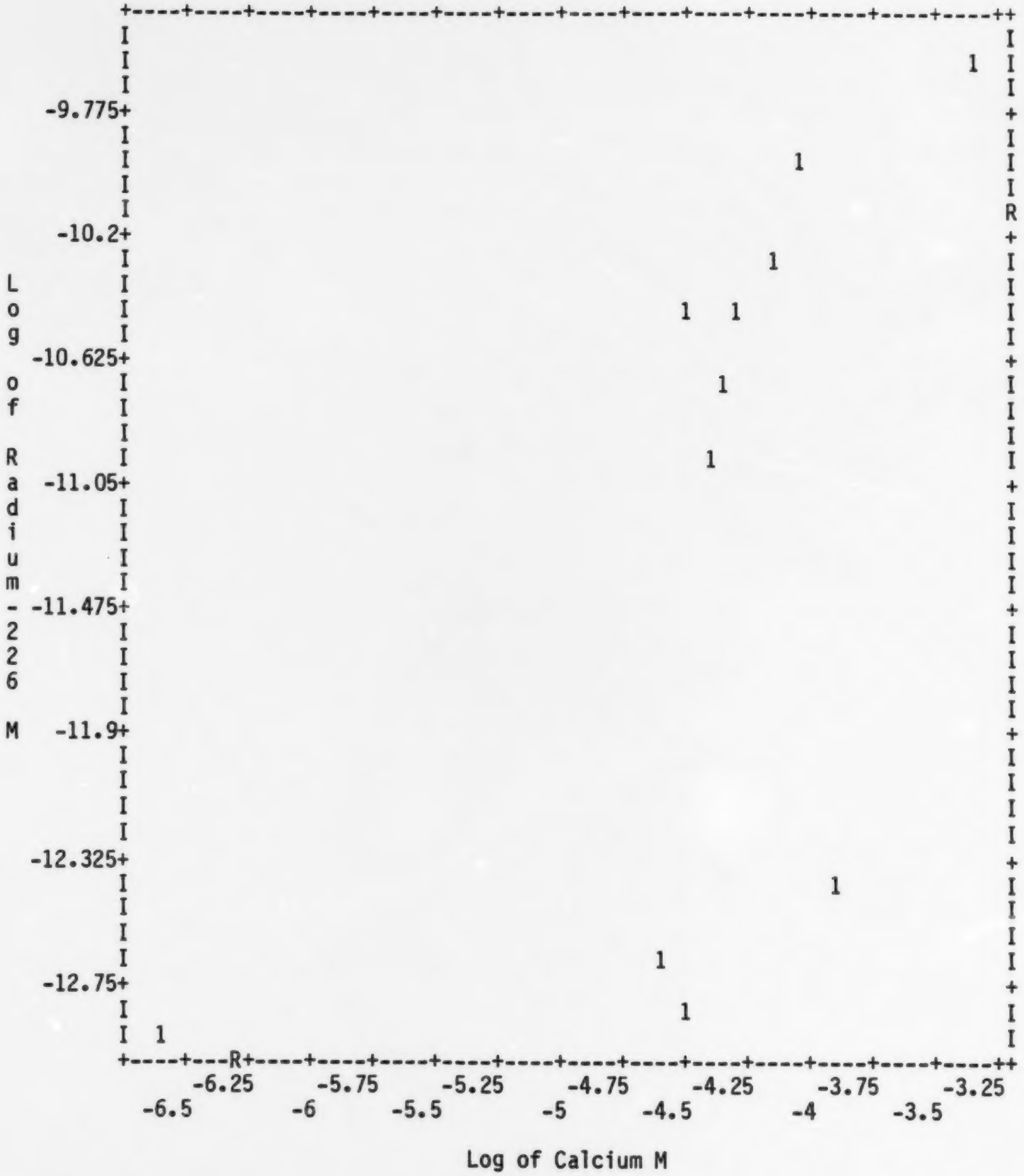
The samples were shipped to Toronto and stored in a moist condition. The solids were divided into 20 or 50 gm lots and contacted with EDTA solutions (10^{-5} M to 10^{-1}M) for 1 hour at S:L ratios of 1:3 and 1:20. The experiment was conducted using a table shaker at room temperature (25°C).

Results

The results are presented in Figure 7.2 (a)-(e) in the form of correlation plots. The plots (Fig. 7.2) and the correlation coefficients (Table 6.4) indicate that Ra-226 is correlated only with barium and lead, albeit the calcium correlation is also reasonable except for 1 outlier.

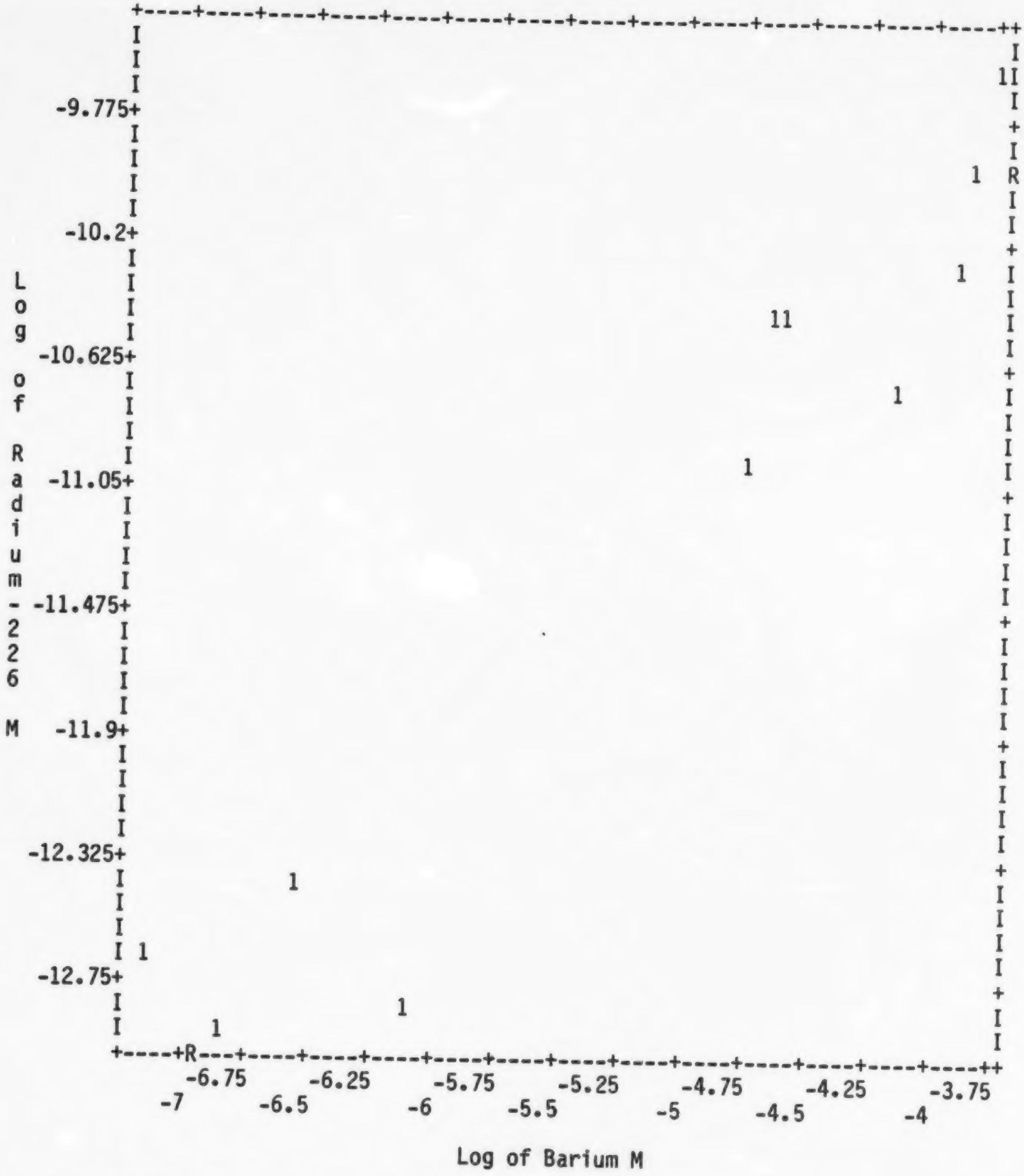
Comparison of the extraction data from these solids which were carefully sampled and immediately filtered with those from the solids which equilibriated with LP liquor for 2 days (section 7.1) shows essentially no difference.

7.2(a) Correlation of Ra with Ca in EDTA Well Washed LP Solids



```
11 cases plotted. Regression statistics of RA on CA:
Correlation  .59600 R Squared  .35521  S.E. of Est    1.04952 Sig.  .0530
Intercept(S.E.)   -7.11947( 1.85949)  Slope(S.E.)     .92061(   .41345)
```

7.2(b) Correlation of Ra with Ba in EDTA Well Washed LP Solids



```
11 cases plotted. Regression statistics of RA on BA:
Correlation  .96153 R Squared  .92454  S.E. of Est     .35903 Sig.  .0000
Intercept(S.E.)    -6.45800(   .46432)  Slope(S.E.)     .92662(   .08824)
```

7.2(c) Correlation of Ra with Sr in EDTA Well Washed LP Solids

```
          +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
          I                                                                      I
          I                                                                   1  I
          I                                                                      I
    -9.775+                                                                      +
          I                                                                      R
          I                                                             1        I
          I                                                                      I
          I                                                                      I
     -10.2+                                                                      +
          I                                                             1        I
 L        I                                                                      I
 o        I                             1  1                                     I
 g        I                                                                      I
   -10.625+                                                                      +
 o        I                                                            1         I
 f        I                                                                      I
          I                                                                      I
 R        I                     1                                                I
 a  -11.05+                                                                      +
 d        I                                                                      I
 i        I                                                                      I
 u        I                                                                      I
 m        I                                                                      I
 - -11.475+                                                                      +
 2        I                                                                      I
 2        I                                                                      I
 6        I                                                                      I
          I                                                                      I
 M   -11.9+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
   -12.325+                                                                      +
          I  1                                                                   I
          I                                                                      I
          I                                                                      I
          R                                1                                     I
    -12.75+                                                                      +
          I                             1                                        I
          I  1                                                                   I
          +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
         -6.625    -6.375    -6.125    -5.875    -5.625    -5.375    -5.125
                -6.5    -6.25         -6    -5.75      -5.5     -5.25        -5

                                    Log of Strontium M

11 cases plotted. Regression statistics of RA on SR:
Correlation  .76591 R Squared  .58662  S.E. of Est     .84034 Sig.  .0060
Intercept(S.E.)   -1.70303(  2.66935)  Slope(S.E.)    1.63726(   .45814)
```

7.2(d) Correlation of Ra with Fe in EDTA Well Washed LP Solids

```
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
         I                                                                      I
         I                                                                     1I
         I                                                                      I
   -9.775+                                                                      +
         I                                                                      I
         I                                                                  1   I
         I                                                                      I
         I                                                                      I
    -10.2+                                                                      +
         I                                                                 1    I
L        I                                                                      I
o        I                                                       2              R
g        I                                                                      I
  -10.625+                                                                      +
o        I                                                              1       I
f        I                                                                      I
         I                                                                      I
R        I                                                  1                   I
a  -11.05+                                                                      +
d        I                                                                      I
i        I                                                                      I
u        I                                                                      I
m        I                                                                      I
- -11.475+                                                                      +
2        I                                                                      I
2        I                                                                      I
6        I                                                                      I
         I                                                                      I
M   -11.9+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -12.325+                                                                      +
         I                                                             1        I
         I                                                                      I
         I                                                                      I
         I1                                                                     I
   -12.75+                                                                      +
         I                               1                                      I
         I                                                 1                    I
         +---+----+--R-+----+----+----+----+----+----+----+----+----+----+----+-+
            -6.325    -5.775    -5.225    -4.675    -4.125    -3.575    -3.025
         -6.6     -6.05      -5.5     -4.95      -4.4     -3.85      -3.3

                                     Log of Iron M
```

```
11 cases plotted. Regression statistics of RA on FE:
Correlation  .68685 R Squared  .47176  S.E. of Est     .94994 Sig.  .0196
Intercept(S.E.)   -8.14215(  1.11580)  Slope(S.E.)      .77682(   .27400)
```

7.2(e) Correlation of Ra with Pb in EDTA Well Washed LP Solids

```
          ++----+----+----+----+----+----+----+----+----+----+----+----+----+----+
          I                                                                      I
          I                                                                     1I
          I                                                                      I
    -9.775+                                                                      +
          I                                                                      I
          I                                                                 1    I
          I                                                                      I
          I                                                                      I
     -10.2+                                                                      +
          I                                                                 1    R
L         I                                                                      I
o         I                                                 2                    I
g         I                                                                      I
   -10.625+                                                                      +
o         I                                                                1     I
f         I                                                                      I
          I                                                                      I
R         I                                               1                      I
a   -11.05+                                                                      +
d         I                                                                      I
i         I                                                                      I
u         I                                                                      I
m         I                                                                      I
-  -11.475+                                                                      +
2         I                                                                      I
2         I                                                                      I
6         I                                                                      I
          I                                                                      I
M    -11.9+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
   -12.325+                                                                      +
          I                                                                1     I
          I                                                                      I
          I                                                                      I
          I 1                                                                    I
    -12.75+                                                                      +
          I                     1                                                I
          I                         1                                            I
          ++----+-R--+----+----+----+----+----+----+----+----+----+----+----+----+
           -6.075    -5.625    -5.175    -4.725    -4.275    -3.825    -3.375
        -6.3     -5.85      -5.4     -4.95      -4.5     -4.05      -3.6

                                       Log of Lead M

11 cases plotted. Regression statistics of RA on PB:
Correlation  .77025 R Squared  .59328  S.E. of Est      .83354 Sig.  .0055
Intercept(S.E.)   -7.30179(  1.10472)  Slope(S.E.)      .93564(   .25823)
```

7.3 EDTA Kinetic Experiment on LP Solids

A kinetic experiment was conducted using the same experimental conditions as the first EDTA washing experiment (section 7.1: mixing by magnetic stirrer; S:L = 1:3, pH = 10, EDTA concentration = 0.1 M, room temperature) and the same leaching pachuca solids (LP12, Dec. 1984 sample). Duplicate solutions were sampled at 5 min., 15 min., 30 min., 45 min., 1 hr., 1.5 hr., 2 hr, and 4 hr. Solution withdrawn for chemical analysis was replaced by an equivalent volume of aqueous solution of concentration 0.1 M EDTA.

The results show no significant trend of cation or Ra-226 chemistry with time. A correlation plot (not shown) and the correlation coefficients (Table 6.4) indicate a better Ra-226 relationship with Pb than with Ba, albeit the concentration ranges of barium, lead, and Ra-226 are all quite narrow compared to data of Fig. 6.1 through Fig. 7.2.

7.4 Extraction Experiments with KCl, $CaCl_2$, $BaCl_2$, $FeCl_3$ and Acids on LP Solids

7.4.1 Experimental Methods

Experimental Methods of Extraction with KCl, $FeCl_3$, $CaCl_2$, $BaCl_2$

Solids from LP#1 of Rio Algom (Nordic Mill; December Sampling) were washed twice with distilled water (S:L = 1:3), air dried, divided in 20 or 50 gm lots and contacted with KCl, $FeCl_3$, $CaCl_2$ and $BaCl_2$ solutions in duplicate at various conditions (10^{-4} - 1 M; S:L = 1:3 and 1:20). The experimental conditions and observed radium-226 concentrations are given in Table 7.2. Correlations of Ra-226 with barium and lead are given in Figure 7.3 for extractions involving KCl, $FeCl_3$ and $CaCl_2$, and in Figure 7.4 for extractions involving $CaCl_2$ and $BaCl_2$.

Experimental Methods of Extraction with Acids

Solids from LP#3 (Rio Algom Nordic Mill; December Sampling) were obtained and separated as described previously prior to storage. Sample preparation here was by washing twice with distilled water and air drying. 50 gm lots of the solid were contacted with hydrochloric acid (0.01 M, 1 M), perchloric acid (1 M), nitric acid (1 M), sulphuric acid (1 M) and distilled water in duplicate at a S:L of 1:3. Mixing was by magnetic

7.3(a) Correlation of Ra with Ba in Salt - LP Solid Experiment

```
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
         I                                                                      I
         I                                                               1      R
         I                                                            11 2  1   I
    -9.75+                                                                  1   +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -10.075+                                                                      +
         I                                                                      I
L        I                                                            1         I
o        I                                                       1 1            I
g        I                                                 12                   I
    -10.4+                                                     11               +
o        I                                                1     1               I
f        I                                                1     1               I
         I                                                                      I
R        I                                            1                         I
a -10.725+                                                                      +
d        I                                                                      I
i        I                                                                      I
u        I                                                                      I
m        I                                       1                              I
-  -11.05+                                                                      +
2        I                                                                      I
2        I                                                                      I
6        I                                                                      I
         I                                                                      I
M -11.375+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.7+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -12.025+                                                                      +
         I   1                                                                  I
         I                                                                      I
         +--+---R+----+----+----+----+----+----+----+----+----+----+----+----+--+
             -6.975    -6.525    -6.075    -5.625    -5.175    -4.725    -4.275
          -7.2     -6.75      -6.3     -5.85       -5.4    -4.95      -4.5

                                 Log of Barium M

22 cases plotted. Regression statistics of RA on BA:
Correlation  .95405 R Squared  .91020  S.E. of Est     .17242 Sig.  .0000
Intercept(S.E.)   -5.92056(   .30820)  Slope(S.E.)     .88835(   .06239)
```

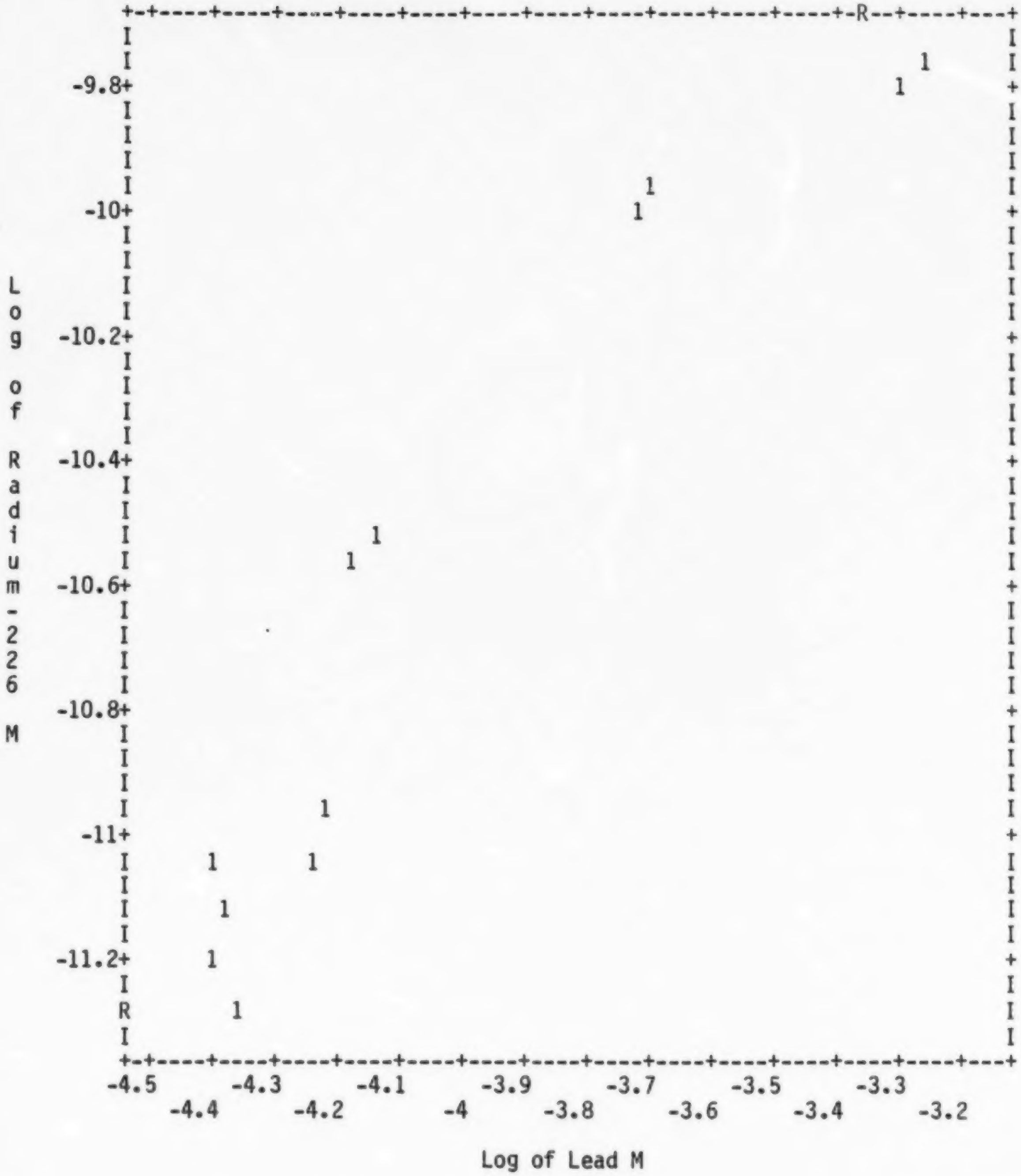
7.3(b) Correlation of Ra with Pb in Salt - LP Solid Experiment

```
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
         I                                                                      I
         I                                                                1     R
         I                                                          1  11 11    I
    -9.75+                                                               1      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -10.075+                                                                      +
         I                                                                      I
L        I                                    1                                 I
o        I                              1       1                               I
g        I                              11      1                               I
    -10.4+                         1             1                              +
o        I                              1                      1                I
f        I                                 1                   1                I
         I                                                                      I
R        I    1                                                                 I
a -10.725+                                                                      +
d        I                                                                      I
i        I                                                                      I
u        I                                                                      I
m        I                                 1                                    I
-  -11.05+                                                                      +
2        I                                                                      I
2        I                                                                      I
6        I                                                                      I
         R                                                                      I
M -11.375+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.7+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -12.025+                                                                      +
         I        1                                                             I
         I                                                                      I
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
             -4.625    -4.375    -4.125    -3.875    -3.625    -3.375    -3.125
        -4.75      -4.5     -4.25        -4     -3.75      -3.5     -3.25

                                     Log of Lead M

22 cases plotted. Regression statistics of RA on PB:
Correlation  .79323 R Squared  .62921  S.E. of Est     .35036 Sig.  .0000
Intercept(S.E.)   -6.54040(   .64580)  Slope(S.E.)     .98852(   .16968)
```

7.4(a) Correlation of Ra with Ba in Calcium Washing of LP Solids

```
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
         I                                                                      I
         I                         1                                            I
     -9.8+                        1                                             +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                  1   R
      -10+                                                                  1   +
         I                                                                      I
         I                                                                      I
L        I                                                                      I
o        I                                                                      I
g   -10.2+                                                                      +
         I                                                                      I
o        I                                                                      I
f        I                                                                      I
         I                                                                      I
R   -10.4+                                                                      +
a        I                                                                      I
d        I                                                                      I
i        I                                             1                        I
u        I                                             1                        I
m   -10.6+                                                                      +
-        I                                                                      I
2        I                                                                      I
2        I                                                                      I
6        I                                                                      I
    -10.8+                                                                      +
M        I                                                                      I
         I                                                                      I
         I                                                                      I
         I     1                                                                I
      -11+                                                                      +
         R     1                          1                                     I
         I                                                                      I
         I 1                                                                    I
         I                                                                      I
    -11.2+ 1                                                                    +
         I                                                                      I
         I                      1                                               I
         I                                                                      I
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
              -5.225    -4.675    -4.125    -3.575    -3.025    -2.475    -1.925
           -5.5     -4.95      -4.4     -3.85      -3.3     -2.75      -2.2

                                     Log of Barium M

12 cases plotted. Regression statistics of RA on BA:
Correlation  .63345 R Squared  .40126  S.E. of Est     .47590 Sig.  .0270
Intercept(S.E.)   -9.41864(   .47630) Slope(S.E.)     .28440(   .10986)
```

7.4(b) Correlation of Ra with Pb in Calcium Washing of LP Solids



```
12 cases plotted. Regression statistics of RA on PB:
Correlation  .95349 R Squared  .90913  S.E. of Est      .18540 Sig.  .0000
Intercept(S.E.)   -5.24977(   .53748)  Slope(S.E.)    1.33007(   .13297)
```

stirrer. The observed radium activity and experimental conditions are given in Table 7.2. Correlation results are given in Figure 7.5 for Ra-Ba and Ra-Pb. Correlation coefficients are also given in Table 6.4.

7.4.2 Results

The radium-226 activity in the different solutions is given in Table 7.2. With the exception of barium chloride, one iron chloride sample and sulphuric acid extraction, there is a general trend of an increasing extraction of Ra-226 with increase in ionic strength from 0.01 M to 1 M in the S:L = 1:3 data. The change in ionic strength through its effect on increase in solubility (i.e., decrease in ion activity coefficient with increase in ionic strength) appears to be the main effect. At 1 M, the amount of Ra-226 leached is fairly constant averaging 1750 (± 258) Bq/L Ra-226 (N=14) for all salts and acids except for sulphuric acid. Among the salts and acids, the effectiveness of extraction is $HClO_4 > FeCl_3 > HCl > KCl > HNO_3 > CaCl_2$. This order is different than that of Starik (1968; cf Benes, 1984) which was $H^+ > Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > K^+ > Na^+$ and different again from that of Havlik et al (1968) which was $K^+ > Na^+ > Li^+ = Ca^{2+} = Mg^{2+} > Sr^{2+} = Ba^{2+}$.

Part of the difference is explained by variation in the data and the use of two different solids (LP#1 for KCl, $FeCl_3$, $CaCl_2$; and LP#3 for the acids).

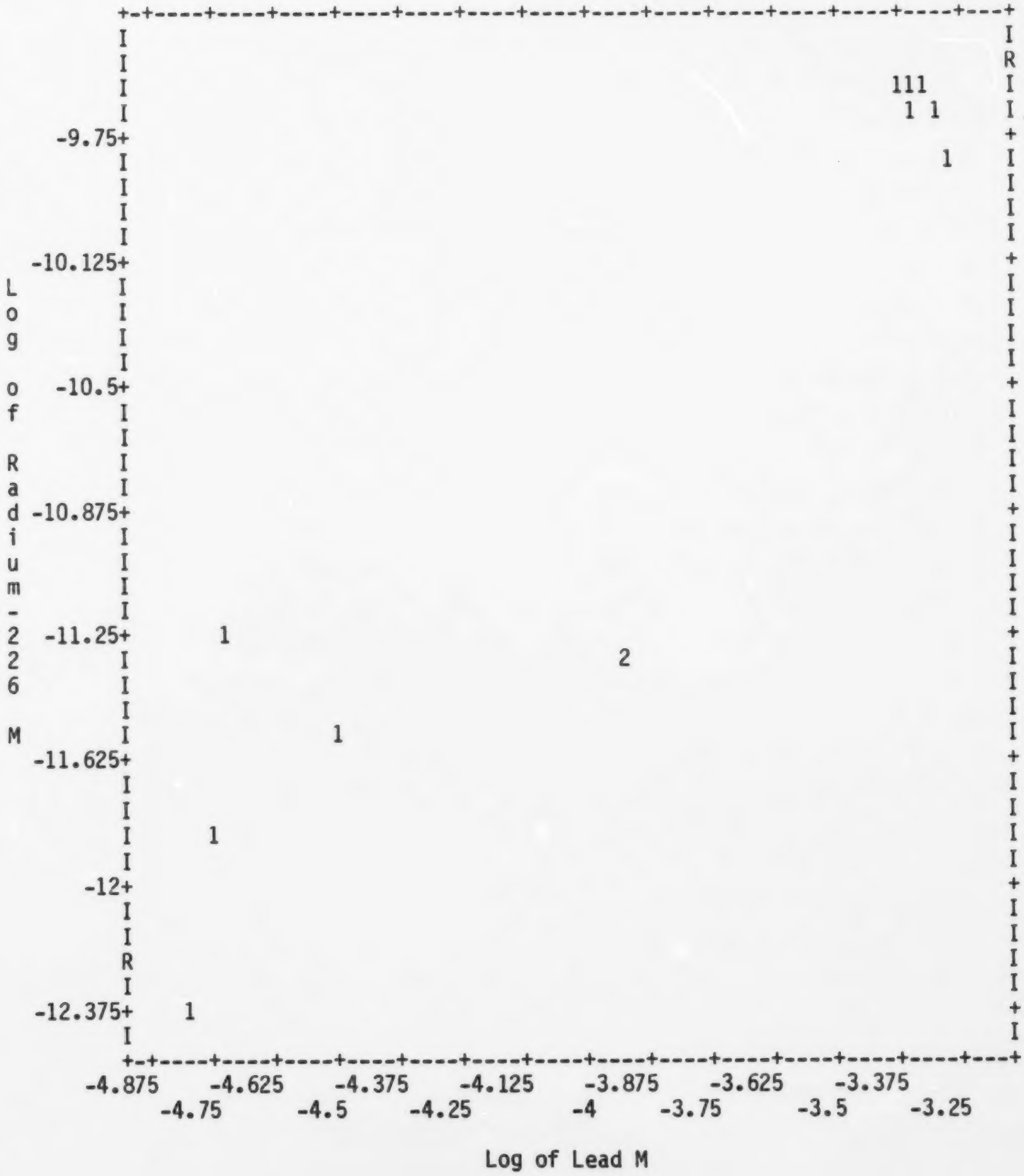
At a S:L of 1:20, the amount of radium-226 extracted appears to be independent of ionic strength. This is a result of the solid:liquid ratio used. The average activity extracted from the 10 solids samples is 135 (±49) Bq while the activity on the solids is 137 ± 7 Bq (2 samples). Hence, the extraction data for the S:L ratio of 1:20 is independent of ionic strength because essentially all of the Ra-226 on the solid phase is dissolved at this S:L ratio.

The value for Ra-226 on the solids is based on measurement of 2 unleached solid samples. The residual Ra226 content of the other leached solids should be measured, but this was not done before the budget was exhausted.

7.5(a) Correlation of Ra with Ba in Acid Washing of LP Solids

```
         +-+----+----+----+----+----+----+----+----+----+----+----+----+----+---+
         I                                                                      I
         I                                                                      R
         I                                                                 12   I
         I                                                                 2    I
    -9.75+                                                                      +
         I                                                               1      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -10.125+                                                                      +
L        I                                                                      I
o        I                                                                      I
g        I                                                                      I
         I                                                                      I
o   -10.5+                                                                      +
f        I                                                                      I
         I                                                                      I
R        I                                                                      I
a        I                                                                      I
d -10.875+                                                                      +
i        I                                                                      I
u        I                                                                      I
m        I                                                                      I
-        I                                                                      I
2  -11.25+                                1                                     +
2        I                             2                                        I
6        I                                                                      I
         I                                                                      I
M        I                            1                                         I
  -11.625+                                                                      +
         I                                                                      I
         I                                                                      I
         I    1                                                                 I
         I                                                                      I
      -12+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -12.375+    1                                                                 +
         I                                                                      I
         +-R----+----+----+----+----+----+----+----+----+----+----+----+----+---+
        -6.975    -6.525    -6.075    -5.625    -5.175    -4.725    -4.275
              -6.75     -6.3      -5.85     -5.4      -4.95     -4.5      -4.05

                                     Log of Barium M

12 cases plotted. Regression statistics of RA on BA:
Correlation  .98693 R Squared  .97403  S.E. of Est     .18019 Sig.  .0000
Intercept(S.E.)   -5.79882(   .25480)  Slope(S.E.)     .95088(   .04910)
```

7.5(b) Correlation of Ra with Pb in Acid Washing of LP Solids



```
12 cases plotted. Regression statistics of RA on PB:
Correlation  .93957 R Squared  .88279  S.E. of Est     .38280 Sig.  .0000
Intercept(S.E.)   -4.59136(   .70446)  Slope(S.E.)    1.55417(   .17908)
```

The effect of barium chloride on extraction is similar to that of other cations, except that barium chloride causes dissolution of a larger amount of Ra-226 than do the other cations at the same ionic strength (see 0.001 M and 0.01 M in Table 7.2). The most direct comparison of the relationship of $BaCl_2$ extraction to the extraction with other salts is an experiment on the same set solids using $BaCl_2$ and $CaCl_2$. The resulting solution concentrations of lead, barium, and Ra-226 are shown in Table 7.3. The Ra-226 data of Table 7.3 are a subset of Table 7.2. Only lead and barium concentrations are given because these are the only cations calculated to be near to saturation with respect to their metal sulphates (see "Equilibrium Calculations" in Section 7.4.3 below). The increase of ionic strength of $CaCl_2$ causes a substantial change in the concentration of lead and barium; the increase of ionic strength of barium chloride causes a similar change in concentration of lead.

The lead concentrations extracted are essentially the same for 10^{-3} M $CaCl_2$ and 10^{-3} M $BaCl_2$. There is a progressive increase in lead concentration over the range of 10^{-4} M to 1 M. This suggests that ionic strength through its effect upon solubility can explain lead dissolution; but ionic strength alone cannot explain the Ra-226 results. It is our suggestion that the larger amount of Ra-226 dissolved using the $BaCl_2$ solution extraction results from its association with a barium sulphate mineral: under higher barium concentrations in solution, a higher rate of interchange between barium in solution and barium in a solid phase results and the solution tends toward a new equilibrium condition between radium in solution and radium in the surface layers of the solid. This point is further addressed in Chapter 11.

7.4.3 Analysis of Data

Correlation Plots

Correlation plots of Ra-226 with Ba and Pb (Fig. 7.3, 7.4, 7.5) indicate that the correlation coefficient is somewhat better for the "Ra-226:barium" relationship than for the "Ra-226:lead" relationship, except for the experiment involving the barium chloride solution (Fig. 7.4). The correlation of Ra-226 with barium for the barium chloride solution should be disregarded because the high solution concentrations of barium result from experimental addition rather than from barium dissolution from the solid. The correlation coefficient, when the barium additions are not considered, is quite good but only involves 4 points.

TABLE 7.3 RADIUM, LEAD AND BARIUM CONCENTRATIONS IN WASHING WATERS USING $BaCl_2$ AND $CaCl_2$

(S:L = 1:3; Time = 1 hr)

	Concentration in Extraction Solution		
Extraction Agent	Pb (mg/L)	Ba (mg/L)	Ra 226 (Bq/L)
10^{-3} M Ca	12.1	0.5	78.3
10^{-3} M Ca	12.4	0.49	90
1 M Ca	105	6.5	1,360
1 M Ca	113	6.8	1,500
10^{-4} M Ba	9.2	-	45.6
10^{-4} M Ba	8.4	-	73
10^{-3} M Ba	13.9	-	225
10^{-3} M Ba	15.1	-	259
10^{-2} M Ba	41	-	924
10^{-2} M Ba	40	-	849

Equilibrium Calculations

Similar speciation-precipitation calculations, as made for the ore leaching data, were made for these data. Of the four plausible metal sulphates (calcium, strontium, barium, lead), the results (see Table 7.4) indicate that the solutions are supersaturated only with respect to barium sulphate. Other solids such as aluminum hydroxide and goethite are calculated to form, but these are not relevant to this discussion. The low percentage of barium which is calculated to precipitate (see Table 7.4) results from the high barium concentration of the washing solution and the low solution sulphate concentrations. The under-saturated nature of the solution with respect to lead sulphate and calcium sulphate reflects the fact that dissolution was still under kinetic control after 1 hour of extracting (mixing) although the solutions were near to, or in excess of, equilibrium conditions with respect to barium sulphate.

7.5 Other Extraction Experiments on Leaching Pachuca Solids

Two other experiments were undertaken on leaching pachuca solids. The first involved washing LP solids with distilled water and then mixing them with 3M $HClO_4$ (S:L = 1:3). Periodically the $HClO_4$ was replaced with a fresh solution of 3M $HClO_4$ (4 hr, 1 day, 2 day, 3 day, and 6 day) and mixing resumed. All solutions were not analyzed, but rather composites analyzed.

Representative results are as follows:

	Pb (mg/l)	Ba (mg/l)	Ca (mg/l)	Sr (mg/l)	Ra (Bq/L)
Distilled (First) Wash	6	.08	203	.41	10.9
$HClO_4$ (T = 4 hr)	104	9.4	5.0	0.69	2121
$HClO_4$ (T = 1-6 day)	9.1	12.5	1.82	0.35	250
7d	1.9	1.7	1.5	0.15	19.8

The results indicate that Ra-226 activity is better correlated with Pb than with Ba suggesting that Pb controls Ra-226 dissolution behaviour. This is counter to the earlier work with EDTA/salt/acid extractions. It would be useful to analyze individually each sample to ascertain its behaviour.

TABLE 7.4 AMOUNT OF METAL (AS A PER CENT) CALCULATED TO PRECIPITATE IN SOLUTIONS RESULTING FROM SALT AND ACID WASHING EXPERIMENTS

7.4 (a) **Washing with KCl, $CaCl_2$ and $FeCl_3$***

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Solid	.01 KCl	.01M KCl	.01M KCl	.01M KCl	1M KCl	1M KCl	1M KCl	1M KCl	.01M $FeCl_3$	.01M $FeCl_3$	1M $FeCl_3$	1M $FeCl_3$	1M $FeCl_3$	.01M $CaCl_2$	.01M $CaCl_2$	1M $CaCl_2$	1M $CaCl_2$	1M $CaCl_2$	1M $FeCl_3$	1M $CaCl_2$
$BaSO_4$	90	71	71	12	30	74	67	0	0	98	44	77	79	0	23	46	63	71	0	0
$PbSO_4$	48	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

• $FePO_4$; $Fe(OH)_3(s)$ $Al(OH)_3(s)$ also calculated to precipitate in a few solutions

7.4 (b) **Washing with $CaCl_2$ and $BaCl_2$***

	1	2	3	4	5	6	7	8	9	10	11	12
Solid	.001M $CaCl_2$	.001M $CaCl_2$	1M $CaCl_2$	1M $CaCl_2$	.0001 M $BaCl_2$	.0001 M $BaCl_2$	.001 M $BaCl_2$	.001 M $BaCl_2$	.01 M $BaCl_2$	.01 M $BaCl_2$	Distilled	Distilled
$BaSO_4$	82	82	0	0	93	90	0.46%	0.47%	.03%	.03%	38	41
$PbSO_4$	0	0	0	0	0	0	0	0	0	0	0	0

• $Al(OH)_3$, $Fe(OH)_3$ also calculated to precipitate

7.4 (c) **Washing with Various Acids**

	1	2	3	4	5	6	7	8	9	10	11	12
Solid	.01 M HCl	.01 M HCl	1 M HCl	1 M HCl	1 M $HClO_4$	1 M $HClO_4$	1 M HNO_3	1 M HNO_3	1 M H_2SO_4	1 M H_2SO_4	Distilled	Distilled
$BaSO_4$	0	0	43	74	81	90	98	99	11	19	38	41
$PbSO_4$	0	0	0	0	0	0	38	77	0	0	0	0

7.4 (d) **Washing with EDTA Solution**

	1	2	3	4	5	6	7	8	9	10
Solid	10^{-5} M EDTA	10^{-4} M EDTA	10^{-4} M EDTA	10^{-3} M EDTA	10^{-2} M EDTA	10^{-2} M EDTA	10^{-1} M EDTA	10^{-1} M EDTA	10^{-1} M EDTA	1M EDTA
$BaSO_4$	87%	89	87	68	0	0	0	0	0	0
$PbSO_4$	0	0	0	0	0	0	0	0	0	0

• $PbCO_3$, $Al(OH)_3$, $Fe(OH)_3$ also calculated to precipitate in a few cases

The other experiment involved sequential washing of LP solids with distilled water (S:L = 1:10). The objective of this experiment was to ascertain if the chemical selectivity caused by the two-order-of-magnitude difference in the solubility constant for $PbSO_4(s)$ and $BaSO_4(s)$ could be used to differentially dissolve Ra-226 and correlate this to the dissolution of the particular parent solid. This experiment was not chemically analyzed for Ra-226 due to exhaustion of the budget.

7.6 Tailings Extraction Experiments on Two NUTP Reference Sites

Gunnar Tailings

Methods

Solids from the Gunnar Tailings site (NIC-S3A-20.22) were obtained from a drill core, returned to the laboratory and washed 4 times with distilled water at a 1:20 ratio for 20 min. per wash. This ratio has been demonstrated in a previous study to bring the conductivity in the last wash water to below approximately 50 uhos. 20 g lots were contacted with EDTA (8 treatments 10^{-5} - 10^{-1} M EDTA; S:L = 1:5 and 1:20); H_2SO_4 (0.01 M, 1 M; S:L = 1:5); HNO_3(0.01 M, 1 M; S:L = 1:5); and KCl (1 M; S:L = 1:5); and distilled water solutions for 1 hour at 25°C using a table shaker.

Results

The results are shown in Fig. 7.6 (a), (b) for Ra-Ba and Ra-Pb correlations and Table 6.4. The relationship of radium with barium is substantially stronger than with lead, suggesting that barium sulphate controls radium-226 behaviour.

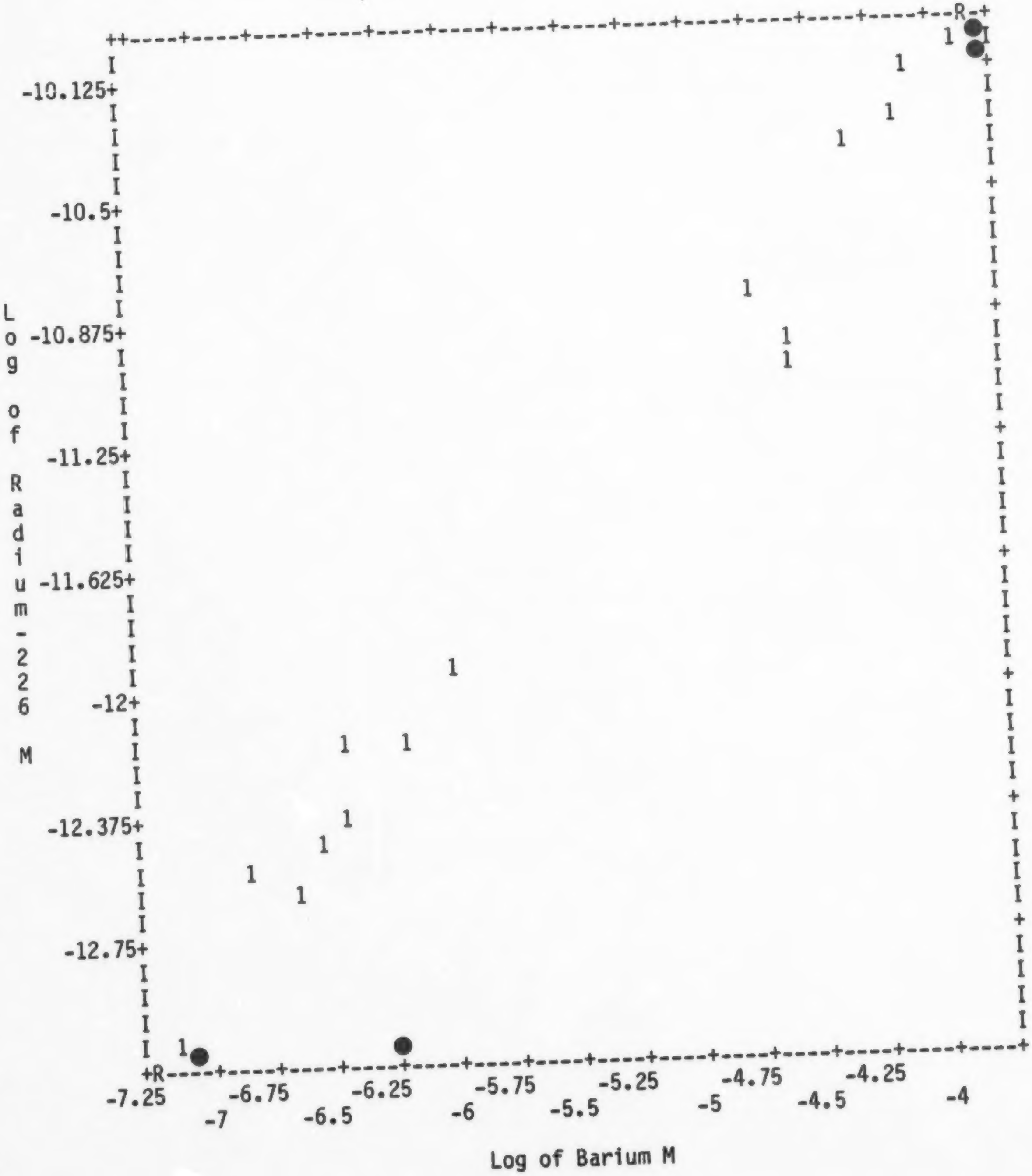
Lacnor Tailings

Methods

Solids from Lacnor (bore hole 85-05; sub-saturated zone) were obtained and prepared in the same way as the Gunnar solids. The same L:S ratios and EDTA/H_2SO_4/HNO_3/KCl treatments were used as with the Gunnar samples.

7.6(a)

Correlation of Ra with Ba from Gunnar Tailings
(EDTA Extraction)

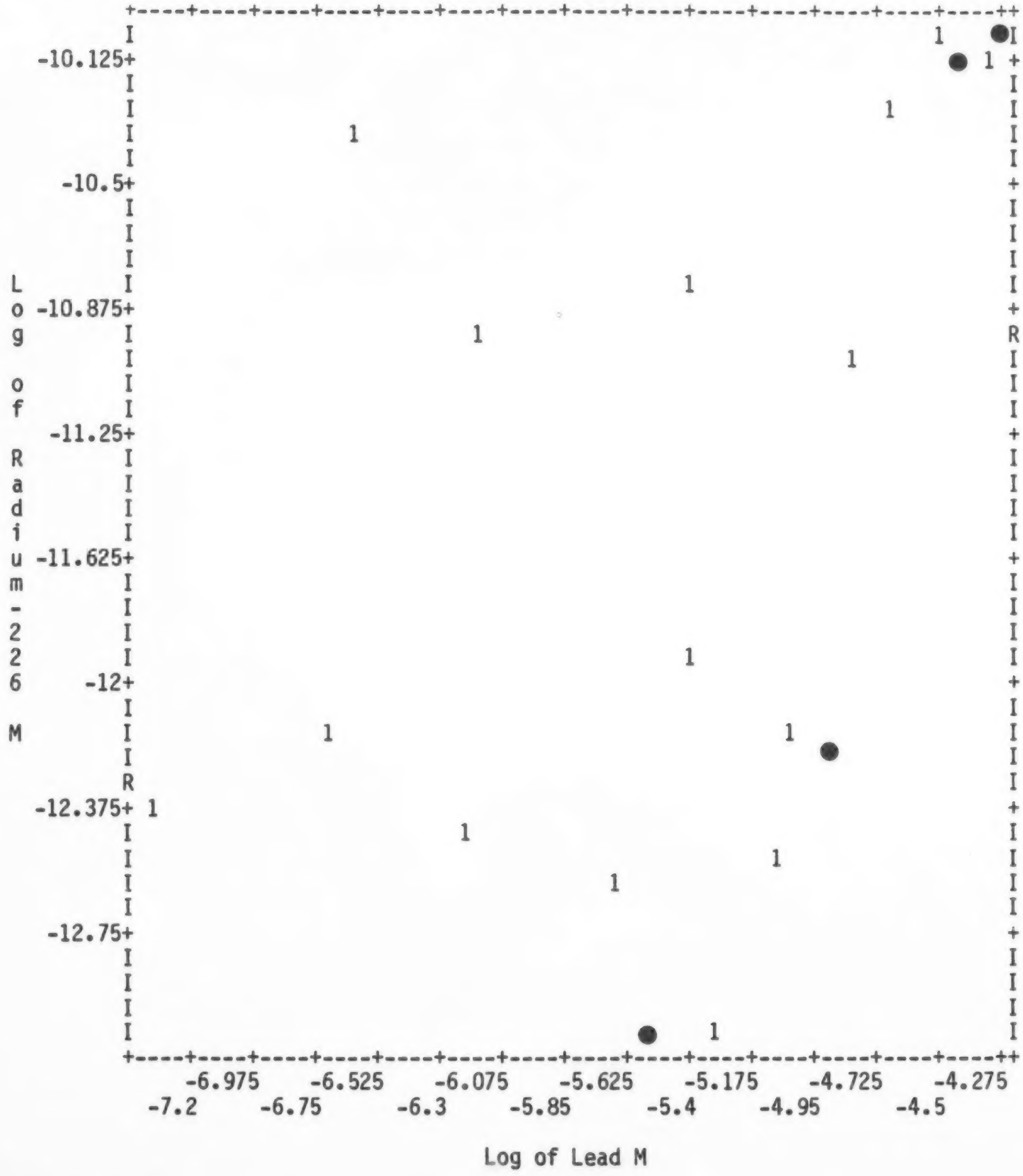


```
15 cases plotted. Regression statistics of RA on BA:
Correlation  .99139 R Squared  .98285  S.E. of Est      .14239 Sig.  .0000
Intercept(S.E.)   -6.65798(  .18203)  Slope(S.E.)      .88301(   .03235)
```

● Langley Bay tailings

7.6(b)

Correlation of Ra with Pb from Gunnar Tailings
(EDTA Extraction)



```
15 cases plotted. Regression statistics of RA on PB:
Correlation  .37478 R Squared  .14046  S.E. of Est    1.00811 Sig.  .1687
Intercept(S.E.)   -9.05846( 1.71169)  Slope(S.E.)      .44429(   .30482)
```

● Langley Bay tailings

Results

The results (Fig. 7.7 a, b for Ra-Ba and Ra-Pb correlations; correlation coefficients given in Table 6.4) indicate that radium activity can be predicted much better by its association with barium ($r^2 = 0.8$) than by lead ($r^2 = 0.3$).

7.7 Extraction Experiments on Other Tailings

Langley Bay Tailings

Methods

Langley Bay tailings were obtained from Station N.5 and contacted directly without washing with EDTA solutions (4 samples, 10^{-5} - 10^{-1} M EDTA, pH = 10; S:L = 1:5; 20 g lot; 25°C) on a table shaker (1 hour contact time).

Results

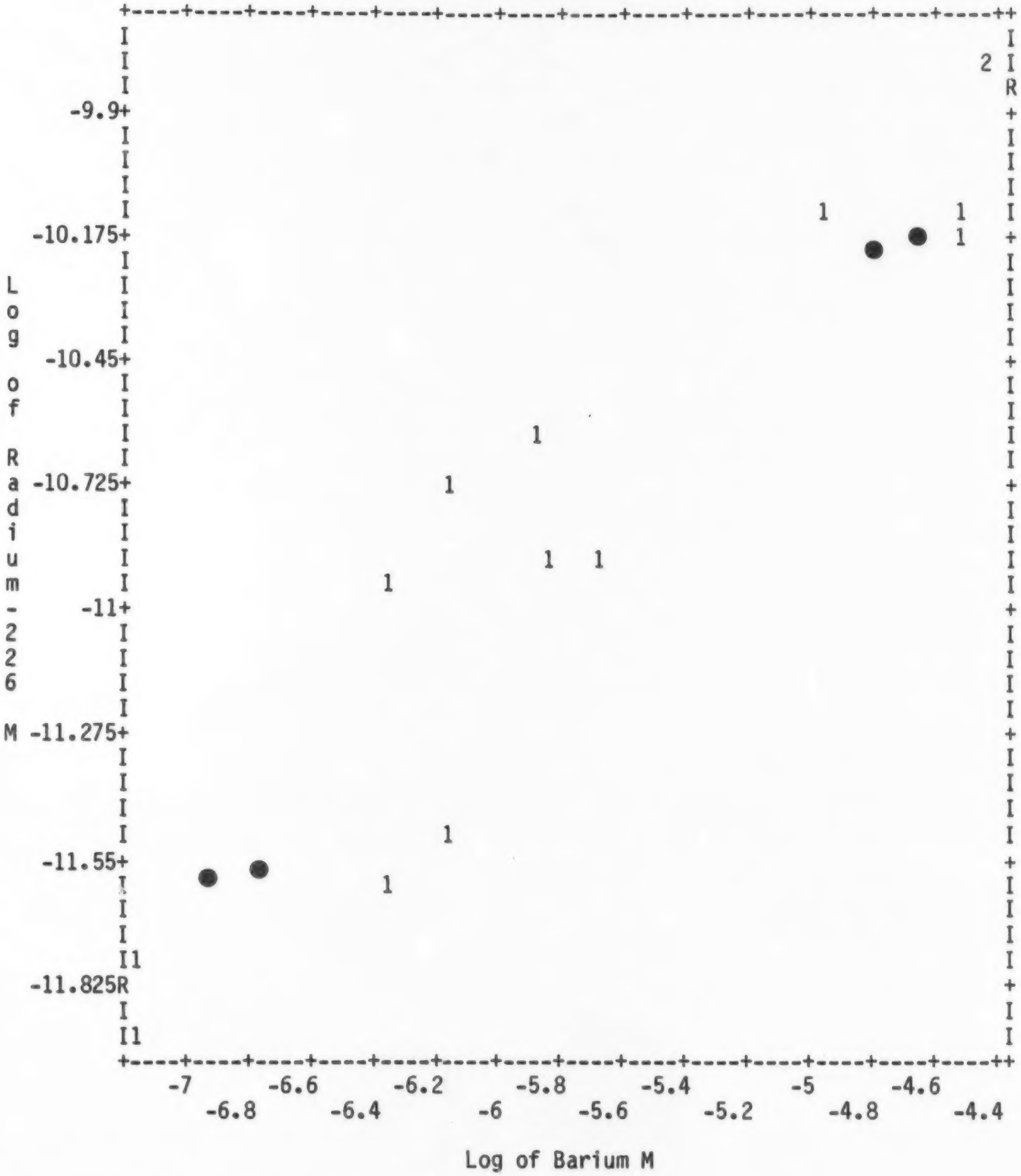
The correlation results (Table 6.4) should not be used to assess whether barium or lead better explain Ra-226 due to only 4 samples being experimentally treated. However, plotting the results on the Gunnar correlation plot (Fig. 7.6) indicate a reasonably similar behaviour between the Gunnar and Langley Bay data factored for the fact that the Langley Bay solids were not washed.

Lacnor Surface Tailings

Methods

Tailings from the same core (85-05) as the above referenced Lacnor tailings but from the unsaturated zone (0.3 m depth) were contacted with EDTA directly without washing. Three samples were extracted with EDTA (10^{-5}M - 10^{-2}M) under the same experimental conditions as the Langley Bay Tailings.

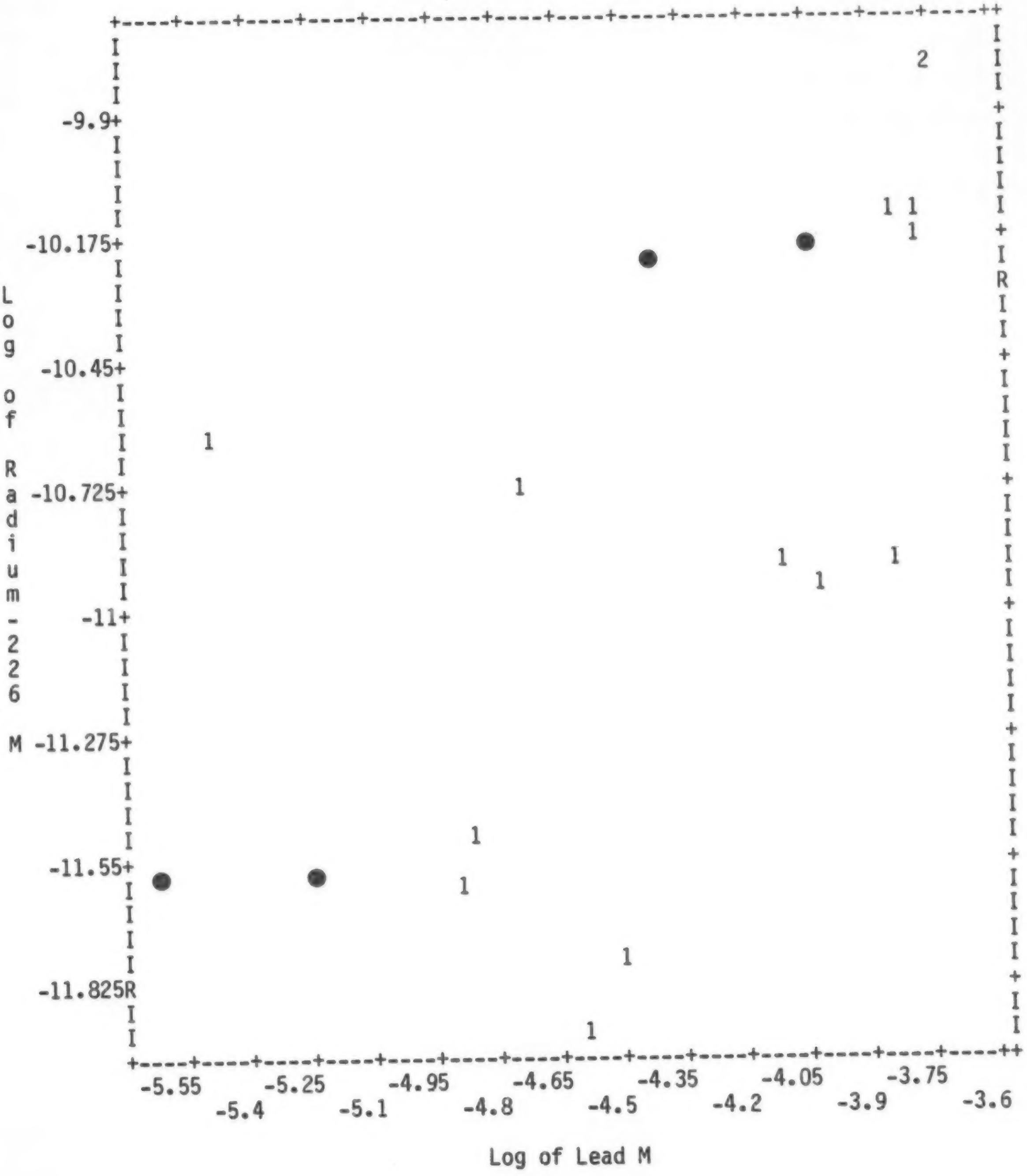
7.7(a) Correlation of Ra with Ba from Lac Nor Tailings
(EDTA Extraction)



```
14 cases plotted. Regression statistics of RA on BA:
Correlation  .94469 R Squared  .89244  S.E. of Est      .24524 Sig.  .0000
Intercept(S.E.)    -6.74579(   .40967)  Slope(S.E.)      .70963(   .07112)
```

● Lacnor (unsaturated zone) tailings

7.7(b) Correlation of Ra with Pb from Lac Nor Tailings
(EDTA Extraction)



```
14 cases plotted. Regression statistics of RA on PB:
Correlation  .59461 R Squared  .35356  S.E. of Est      .60122 Sig.  .0249
Intercept(S.E.)   -7.51693(  1.28419)  Slope(S.E.)      .76215(   .29750)
```

● Lacnor (unsaturated zone) tailings

Results

The results (Table 6.4), plotted on Fig. 7.7 indicate reasonably similar extraction characteristics as with the Lacnor tailings from the saturated zone.

Acid Digestion Experiment Solids

Methods

Solids resulting from the acid digestion experiment treated with 3 M perchloric acid (60°C; 24 hr contact time) were divided into 10 gm lots and contacted directly (without distilled water wash) with EDTA (10^{-5}M - 10^{-2}M; 3,10 g lots) under the same experimental conditions as the Langley Bay sediments.

Results

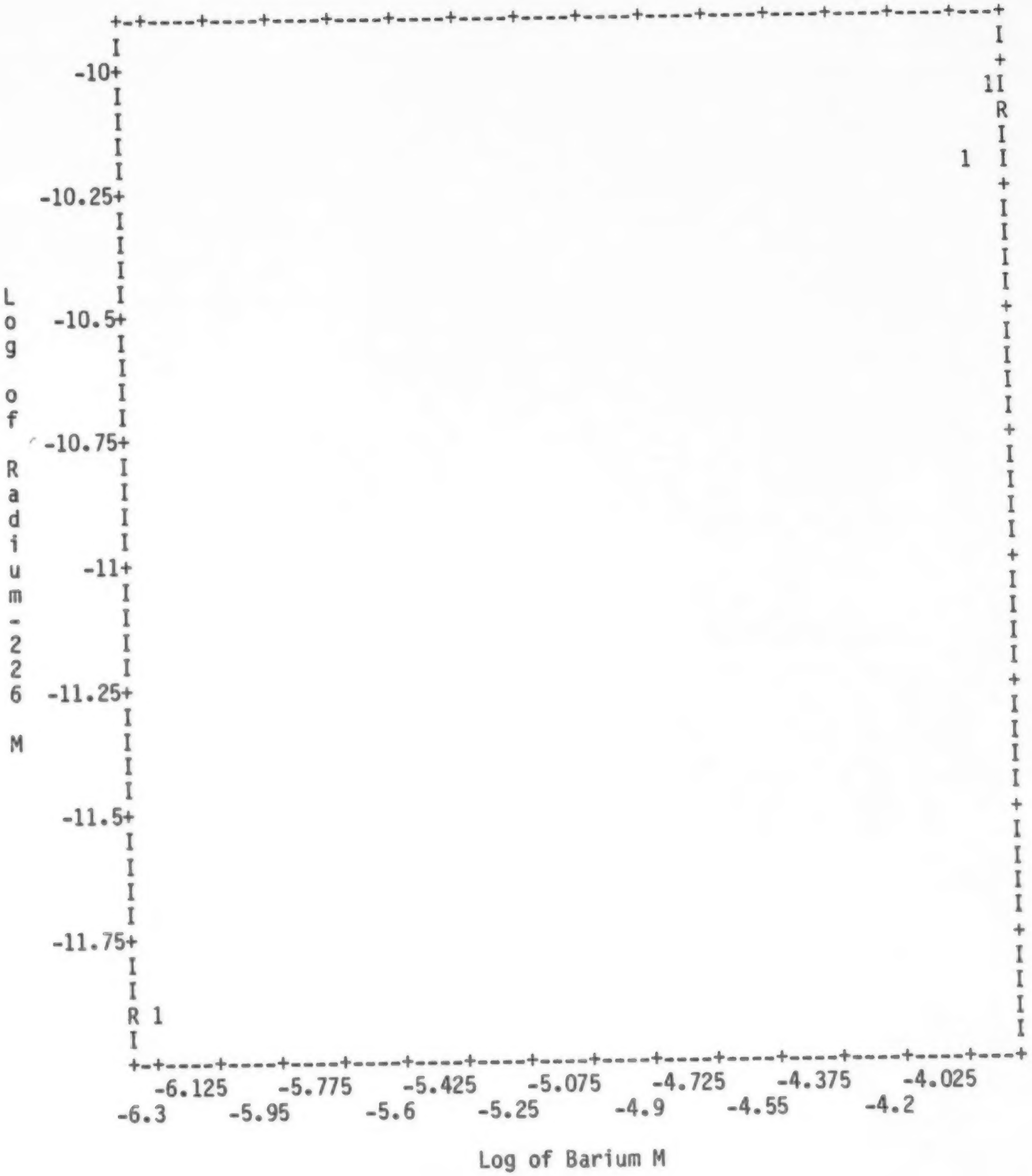
The results are plotted in Fig. 7.8 for Ra-Ba and Ra-Pb and the correlations given in Table 6.4. The equations of the correlations are consistent with those from the other leaching pachuca experimental data, suggesting that the acid digestion experiment reasonably emulates actual leaching pachuca conditions factored for the different acid involved.

Old Nordic Tailings

Methods

3, 10 g samples from the Old Nordic tailings treated previously by EDTA/KCl experimentation (Constable and Snodgrass, 1983) were contacted directly (no distilled water wash) with EDTA (10^{-5} - 10^{-2} EDTA) using the same conditions as for the Langley Bay solids.

7.8(a) Correlation of Ra with Ba from Acid Digestion Solids (EDTA Extraction)



```
3 cases plotted. Regression statistics of RA on BA:
Correlation  .99779 R Squared  .99559  S.E. of Est     .09538 Sig.  .0423
Intercept(S.E.)   -7.15698(   .24272)  Slope(S.E.)     .74980(   .04991)
```

7.8(b) Correlation of Ra with Pb from Acid Digestion Solids (EDTA Extraction)

```
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
         I                                                                      I
      -10+                                                                      +
         I                                                                   1  I
         I                                                                      R
         I                                                                      I
         I                                                                    1 I
   -10.25+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
L        I                                                                      I
o   -10.5+                                                                      +
g        I                                                                      I
         I                                                                      I
o        I                                                                      I
f        I                                                                      I
   -10.75+                                                                      +
R        I                                                                      I
a        I                                                                      I
d        I                                                                      I
i        I                                                                      I
u     -11+                                                                      +
m        I                                                                      I
-        I                                                                      I
2        I                                                                      I
2        I                                                                      I
6  -11.25+                                                                      +
         I                                                                      I
M        I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.5+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
   -11.75+                                                                      +
         I                                                                      I
         I                                                                      I
         R 1                                                                    I
         I                                                                      I
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
            -5.625    -5.375    -5.125    -4.875    -4.625    -4.375    -4.125
        -5.75      -5.5     -5.25        -5     -4.75      -4.5     -4.25

                                      Log of Lead M

3 cases plotted. Regression statistics of RA on PB:
Correlation  .99455 R Squared  .98913  S.E. of Est     .14970 Sig.  .0665
Intercept(S.E.)  -5.82118(   .51946) Slope(S.E.)    1.04862(   .10991)
```

Results

The results, plotted on the original diagrams, (See Fig. 2.1 (a) - (d)), indicate that the extraction is consistent with that obtained experimentally two years ago (Jan. 1983). This supports the hypothesis advanced then that Ba controls Ra-226 dissolution and that (Ba, Ra)SO_4 controlling Ra-226 behaviour has remained intact in the tailings sample for the past two years.

8.0 ADSORPTION EXPERIMENT

8.1 Experimental Methods

An aliquot of the leaching pachucas solids (Feb. sampling, LP #12) used for the well-washed LP experiment (with EDTA), was chosen for this experiment. The solids were prepared by washing once at a S:L ratio of 1:10 with 1 M KCl and then again at a S:L ratio of 1:5 with 1 M KCl. This procedure is designed to remove most of the Ra-226 coprecipitate on the surface and hence to allow a "true" adsorption experiment.

The required amount of solids was added to 10 ml of acid solution to give three different S:L ratios of 1:40, 1:10, and 1:1 (respectively 0.25 g, 1 g, and 10 g added). Four acid solutions were used: 0.1 M HNO_3, 1 M HNO_3, 0.1 M H_2SO_4, and 1 M H_2SO_4, giving 12 experimental conditions for evaluating adsorption (see Table 8.1). Four (4) replicate jars were set up for each experimental condition: two were spiked with 0.2 ml of Ra-226 chloride stock solution to give approximately 6,500 Bq/L total Ra-226 activity for each spike; two were treated as blanks (not spiked), with one used for cation analysis and one used for Ra-226 analysis.

The samples where shaken for 1 hr with a wrist action shaker and then the solids were separated from this liquid using a 3,500 rpm centrifuge. The decanted supernatant was then centrifuged at 10,000 rpm. The second centrifugation showed the accumulation of a small white deposit estimated to be 0.1 mg or less in weight. This white deposit is assumed to consist of surface precipitates from the leaching pachuca solids not dissolved by the KCl washing and removed from the larger solids by mechanical abrasion during shaking.

8.2 Results

The results are given in Table 8.1. The residual Ra-226 activity in solution of the duplicates spiked with Ra-226, and the Ra-226 activity and Pb and Ba concentrations in the blanks are given in Table 8.1(a). The Pb and Ba concentration are assumed to be representative of their concentration in the solutions spiked with $RaCl_2$. The values of the linear adsorption coefficient (K_D) calculated from these data are given on Table 8.1(b).

TABLE 8.1a

RESULTS OF ADSORPTION EXPERIMENT
AND Pb AND Ba CONCENTRATION

a) Radium Activity in Solution after Adsorption Experiment

S:L	0.1 M HNO_3			1 M HNO_3			0.1 M H_2SO_2			1 M H_2SO_4		
	Ra 226	Pb	Ba	Ra 226	Pb	Ba	Ra 226	Pb	Ba	Ra 226	Pb	Ba
1:40												
Residual in Solution	6,630 (± 680)			6,297 (± 83)			1,467 (± 830)			1,182 (± 112)		
Residual in Blank	23.2	0.45	0.91	23.9	1.06	0.89	9.3	0.25	0.04	5.7	.38	.03
1:10												
Residual in Solution	5,697 (± 986)			5,539 (± 70)			621 (± 9)			886 (± 158)		
Residual in Blank	171	2.3	2.4	78.9	4.0	1.8	17.7	1.1	0.2	12.0	1.29	0.28
1:1												
Residual in Solution	6,146 (± 630)			5,462 (± 513)			4,880 (± 393)			2,155 (-)		
Residual in Blank	201	24	3.6	263	34	2.2	113	20	1.9	205	21	1.36

Standard: 6,517 (± 619)

Precision on Duplicate Counts

1. 834 ± 0 (N = 2)
2. 2,100 ± 87 (N = 2)
3. 1,049 ± 8 (N = 2)
4. 789 ± 59 (N = 2)

TABLE 8.1b CALCULATED VALUE OF K_D (ml/gm)**

S/L Ratio	Solution			
	0.1 M HNO_3	1 M HNO_3	0.1 M H_2SO_4	1 M H_2SO_4
1:40	0*	1.4*	140	180
1:10	1.4*	1.8*	95	64
1:1	0.06*	0.2*	0.33	2.0

** Linear sorption coefficient (K_D) defined as amount sorbed on solids (Bq/gm) divided by solution activity (Bq/ml)

* Amount adsorbed is not significantly different from 0. Hence K_D is considered as not different from zero.

For the nitric acid solution, the calculated values of K_D vary from 0 - 2 ml/g. But analysis of the amount of Radium absorbed shows that it is not statistically different from zero at the 95% Confidence Interval (CI). Hence the value of K_D is approximately zero for the nitric acid solutions.

For the sulphuric acid solutions, K_D has values of approximately 160 ml/g at a S:L = 1:40; 80 ml/g at a S:L = 1:10 and 1.2 ml/g at a S:L = 1:1, for the pH range of 0 - 1. There is no discernable effect upon K_D in going from 0.1 M H_2SO_4 to 1 M H_2SO_4 solutions.

8.3 Discussion

The main contrasts in K_D are the differences caused by the S:L ratios and the differences between the acids. It is our hypothesis that the "calculated value of K_D" results from the effects of coprecipitation with barium sulphate in sulphuric acid solution rather than reversible adsorption. This hypothesis should be tested using desorption experiments, but the timing of contract completion precluded this experiment.

The data of Table 8.1a support the hypothesis although measurement of sulphate in the nitric acid solutions would be useful to lend further support to this hypothesis. The lead concentrations in the blank mirror the S:L ratios used: as the volume of liquid used per gm of solids increases 10 times and 40 times, the concentrations of lead decrease approximately 10 times and 40 times. This suggests that the ionic strength of the acid solution through its effect upon solubility is large enough to dissolve all residual Pb, not removed by the KCl wash. This effect upon Pb is the same in both acidic solutions because there are essentially no differences in the concentration of Pb in the nitric acid and sulphuric acid solutions.

The Ra-226 and Ba concentration in the blanks of the nitric and sulphuric acid solution show a different pattern than does Pb. The barium concentrations are essentially the same in the 1:1 and 1:10 HNO_3 solutions, but decrease by approximately 50% in the 1:40 HNO_3 solutions. This suggests that barium saturation is maintained in the 1:1 and 1:10 experiments but not in the 1:40 solution. We need to measure sulphate concentrations in the nitric acid solutions to confirm this point quantitatively.

In the sulphuric acid solutions, the barium concentrations in the blank decrease approximately in proportion to the dilution of the L:S ratio. The reason for this cannot be explained on the basis of simple solubility, because the sulphate concentrations are essentially constant as the S:L ratio is varied from 1:1 to 1:40. Furthermore, in the 1:1, S:L ratio in 1 M H_2SO_4 solution, the calculated degree of saturation is over 100 with respect to $BaSO_4(s)$; the 1:40 ratio in 1 M H_2SO_4 is closer to equilibrium but its degree of supersaturation is still approximately 7-10 times saturation (depending upon the values assigned to the activity coefficients).

This relationship of decreasing K_D with increasing solids concentration has been observed so extensively elsewhere (e.g., DiToro and Connelly, 1980; Rao et al, 1982; DiToro and Horzempa, 1982) that people often use such relationships in modelling work for adsorption of inorganic and organic substances onto soils and geological materials. However, it theoretically should not exist. Factors explored to explain this phenomena include a change in surface area; complexation and adsorption of the complexes; and formation of a "mysterious" third phase which desorbs from the solid to keep sorbing elements in solution. None of these factors has been successful in explaining the observations.

A possible explanation suggested by these data is based upon kinetic concepts. The effect of ionic strength upon the activity coefficient appears to be successful in explaining the rapid dissolution of barium sulphate. The role of hydrogen ion substitution for barium within a $BaSO_4$ lattice is possible, but is probably ruled out by the results of experiments on similar LP solids where other cations (KCl, $CaCl_2$, $FeCl_3$) gave essentially the same extraction characteristics as hydrogen ion (perchloric, nitric, hydrochloric acids). The rate effect cannot be due to inadequate surface area because the experiment containing the largest relative surface area (S:L = 1:1) is the one with the highest barium concentration in solution. Nor can the rate effect be directly due to degree of supersaturation because higher precipitation rates are expected at higher degrees of supersaturation whereas the experiment having the highest degree of supersaturation (S:L = 1:1) has the highest barium concentration and hence the lowest precipitation rate.

It is postulated that the rate effect can be explained by a parameter defined as the "degree of supersaturation per unit surface area per ml of solution". An analogous parameter can be defined as the "barium concentration in solution (e.g., mg/L) per unit surface area density (cm^2 of surface/L)". Both parameters allow an estimate of the chemical tendancy of the solution to induce nucleation and crystal growth when account is taken of the different surface area involved. These parameters are in addition to the normal parameter of supersaturation ratio which assumes that the rate of precipitation is independent of surface area. Such a parameter has been analyzed in other precipitation studies. For both parameters, their relative values are 1 for the S:L = 1:40, 1.6 for S:L = 1:10 and 1 for S:L = 1:1. Hence within the limits of the variability of the data, it is judged that the chemical driving force for formation of $BaSO_4$ is the same in all solutions and hence that the rate of precipitation has been the same in all solutions.

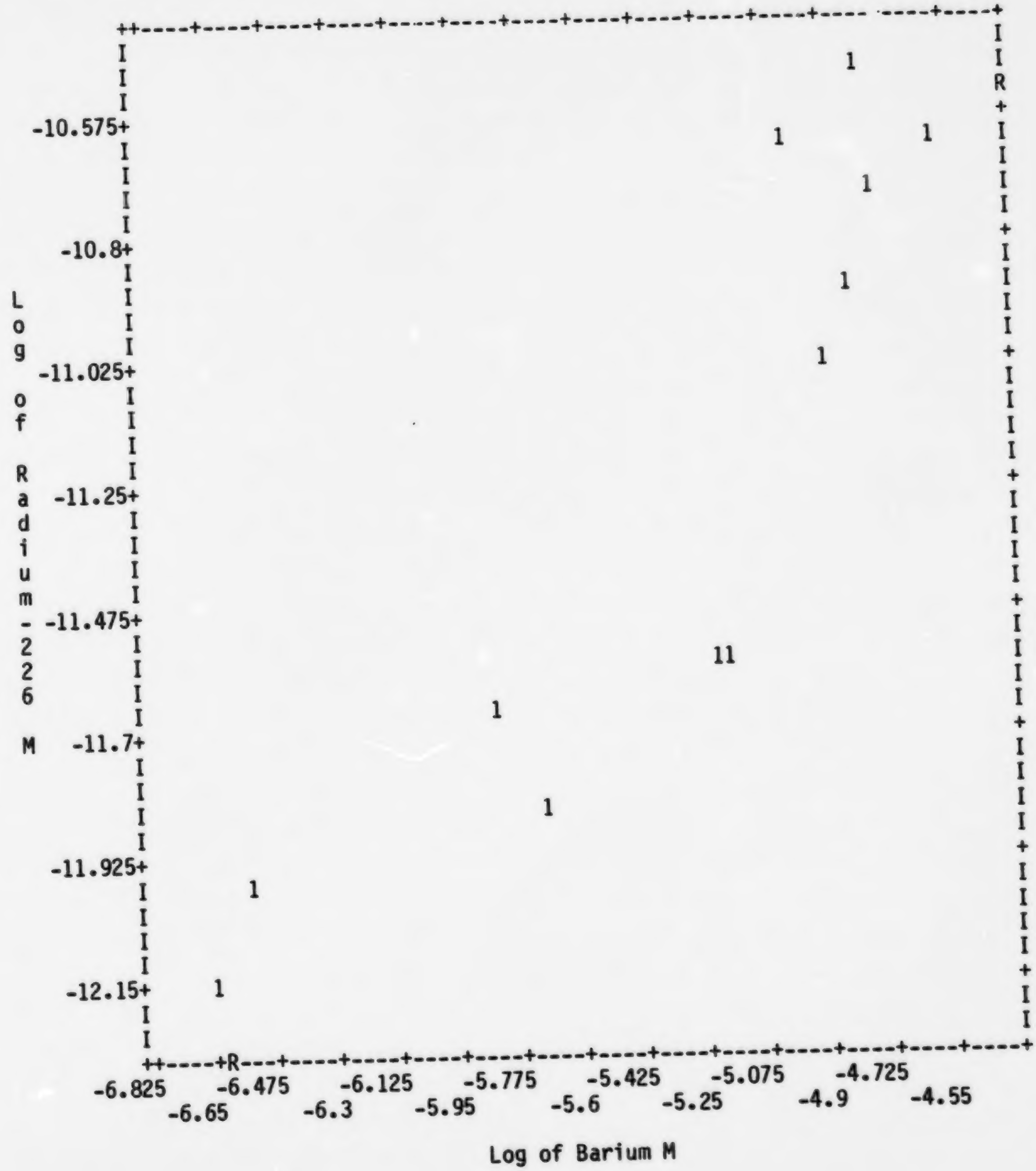
A correlation analyses of Ra-226 in the blanks with Ba and with Pb (Figure 8.1) shows a similar strength relationship of Ra-226 with Ba as with Pb.

The Ra-226 activity in the nitric acid blanks respectively represent 0.23 Bq/q (6.3 p Ci/g); 1.23 Bq/g (30 p Ci/g); and 0.59 Bq/g (16 p Ci/g) in the solutions of S:L = 1:1, 1:10 and 1:40. This points out that the KCl washing was nearly successful in cleaning all of the Ra-226 from the solids.

The higher "K_D" value for Ra-226 in the S:L = 1:40 compared to that in the S:L = 1:1 H_2SO_4 solutions suggests that the Ra-226 precipitation kinetics are much more rapid in the former solutions. The degree to which the above hypothesis can explain the values of K_D will await future work. The hypothesis given above suggests that, in fact, the coprecipitation kinetics of Ra-226 are constant when one takes acount of the different surface areas on the solutions. A useful experiment to examine this hypothesis would be the use of longer contact time, particularly for the 1:10 and 1:1 S:L ratios, and desorption experiments.

It will also be quite useful to see how far these coprecipitation ideas versus competitive adsorption ideas could be used to explain the K_D-solids relationships observed in other systems. For some cation systems which are not supersaturated with respect to the

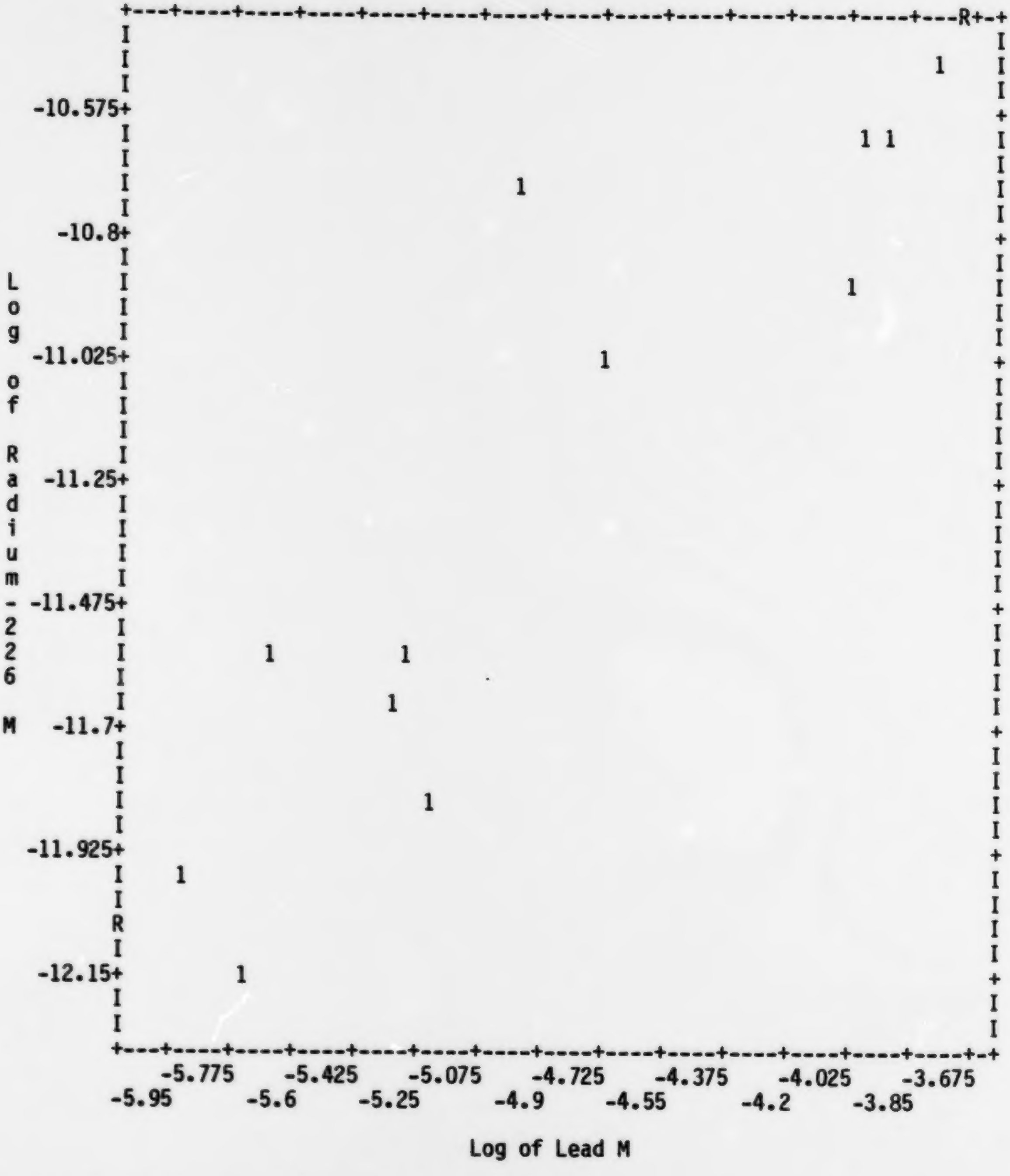
8.1(a) Correlation of Ra with Ba in Blanks of Adsorption Experiment



```
12 cases plotted. Regression statistics of RA on BA:
Correlation  .89316 R Squared  .79774  S.E. of Est    .28169 Sig.  .0001
Intercept(S.E.)   -7.18095(   .65353)  Slope(S.E.)    .76352(   .12157)
```

8.1(b)

Correlation of Ra with Pb in Blanks of Adsorption Experiment



```
12 cases plotted. Regression statistics of RA on PB:
Correlation  .89973 R Squared  .80951  S.E. of Est     .27337 Sig.  .0001
Intercept(S.E.)   -7.85573(   .52715)  Slope(S.E.)     .69662(   .10686)
```

adsorbing ions, coprecipitation may be the appropriate explanation. The lack of characterization of other cations in these systems described in the literature, limits one's ability to examine these observations.

8.4 Analysis of Literature Data

Our experimental adsorption data point out the need to carefully assess literature data describing adsorption of Ra-226 onto various geological materials. For example, Gillham et al (1981) measured K_D values for barium of 60 to 3,500 ml/gm and for radium of 50 to 1,000 ml/gm when sorbed onto various soils at neutral pH (range of 7-9). Their objective was to see whether barium could be used to predict Ra behaviour in laboratory experiments based upon similarity of charge, ionic radius etc. They conclude that barium could not be used to predict Ra behaviour, partly because barium behaviour in adsorption studies is influenced by the amount of barium occurring naturally in the soil (barium as a coprecipitate in magnesium and calcium carbonates).

They kept the radium concentration low enough to prevent precipitation of its carbonate and sulphate, but added chloride salts of magnesium, calcium, sodium and potassium equal to the amount of the respecive cations that desorbed from the soils in control experiments. They do not report barium concentrations in these solutions, but it is possible that $BaSO_4$ and/or $BaCO_3$ or other precipitates could form and coprecipitate Ra-226. For example, for their soil with an equilibrating solution concentration for Ca of 2020 mg/L (0.05 M; Pg B.14 of Gillham et al, 1981) and sulphate of 1×10^{-3} M, the solution is subsaturated with respect to gypsum by approximately 50%. But if 0.1 mg/L of barium desorbed, the solution would be supersaturated with respect to $BaSO_4$ by approximately 3-5 times.

This example points out the need to measure all relevant solution cations and anions in any future experiments, in order to assess the potential for coprecipitation to influence "sorption".

9.0 SYNPOSIS OF EXPERIMENTAL RESULTS

The hypotheses of this research are developed in the first few chapters and summarized in Chapter 5.0. Briefly, the hypotheses can be summarized as "Ra-226 dissolution behaviour in uranium mill tailings is controlled by dissolution of a mixed crystal formed in the sulphuric acid solutions of the leaching pachucas of the uranium mill". This chapter summarizes the experimental evidence developed to substantiate the postulate and further analyzes the data. A later chapter (11) evaluates the experimental data of Chapters 6-8 using thermodynamic concepts for coprecipitation phenomena.

9.1 Evaluation of Mill Operating Data

For a coprecipitate to form, the solutions in the leaching tanks should be supersaturated with respect to the parent crystal, and relationships of cations and radiocations in solution should mirror those in the mixed crystal formed upon the solid phase. The supersaturation conditions and leaching solution relationships have been evaluated in detail in Chapter 6 and are summarized here. Solid-solution relationships are evaluated in Chapter 11.

The mill operating data show the following:

(i) The leaching liquor solutions are supersaturated with respect to $BaSO_4(s)$, $PbSO_4(s)$, and $CaSO_4.2H_2O(s)$ but not with respect to $SrSO_4(s)$. Saturation conditions with respect to jarosite were not evaluated. This suggests that only barite, anglesite, or gypsum are plausible mixed crystals for controlling Ra-226 dissolution behaviour in the leaching pachucas.

(ii) Relationships are observed for the activity of Ra-226 in leaching solutions with the concentration of Ba and Pb, but not with the concentration of Ca. This suggests that Ra-226 behaviour may be controlled by the formation of barite and/or anglesite.

(iii) One can determine the expected activity of Ra-226 and Ra-228 in solution in the leaching pachucas based on the amount of uranium 238 and/or thorium (230, 232) in solution and the ratio of Ra-226 or Ra-228 to its parent radionuclide (respectively U-238 and Th-232) in the host mineral. Comparison of the expected activity to the observed activity in solution indicates that there is a smaller ratio (observed/expected) of Ra-226 in solution than of Ra-228. But chemically there should be a similar ratio if both undergo coprecipitation reactions at the same rate. The different ratios suggest that the nucleation site(s) for mixed crystal formation are physically much closer to the uranium-containing mineral(s) (e.g., uraninite/bannerite) than to the thorium-containing mineral(s) (e.g., monazite), or that the dissolution kinetics of uranium-minerals are faster than thoughs of thorium-minerals.

9.2 Evaluation of Dissolution Studies on Leaching Pachucas and Tailings Solids

This section summarizes relationships between Ra-226 and various cations in dissolution studies observed in Chapter 7 and extends the analysis by examining all experimental data (except for the adsorption experiments) and subsets of this data.

Correlation analyses between Ra-226 and various cations in dissolution experiments have been presented in Chapter 7 for each individual experiment. The correlations indicate the following:

(i) Ra-226 dissolution is correlated with barium dissolution; Ra-226 dissolution is also correlated with lead dissolution. The degree of correlation is generally better with barium than with lead as measured by the coefficient of determination (r^2). There is a small difference in r^2 for Ra-Ba and Ra-Pb correlations on leaching pachuca solids, but r^2 is substantially larger for Ra-Ba correlations on the tailings solids than for Ra-Pb correlations.

(ii) Ra-226 dissolution is not correlated with the dissolution of calcium, strontium, or iron if a minimum value for r^2 is used as a criterion. A discussion of useful values of r^2 are given in the appendix.

The results suggest that only mixed crystals of barite or anglesite control Ra-226 dissolution from the leaching pachuca solids or from the tailings.

Analysis of All Experimental Data and Subsets

Correlation plots of Ra-226 with barium and lead are given for all acid digestion data (laboratory; mill from Chapter 6) in Fig. 9.1; for all data from dissolution experiments upon leaching pachuca solids (Chapter 7) in Fig. 9.2 and 9.3; and for all tailings data (Chapter 7) in Fig. 9.4. Correlation plots for Ra-226 with the other cations (Ca, Ba, Sr, Fe Pb) are given for the tailings solids in Fig. 9.4 and for all experimental data (Fig. 9.5). The plots of Ra-226 with Ca, Sr, and Fe are almost a perfect scattergram for both the tailings experiments (Fig. 9.4) and for all experimental data (Fig. 9.5). This reinforces the earlier findings that only Ba or Pb can explain the dissolution behaviour of Ra-226.

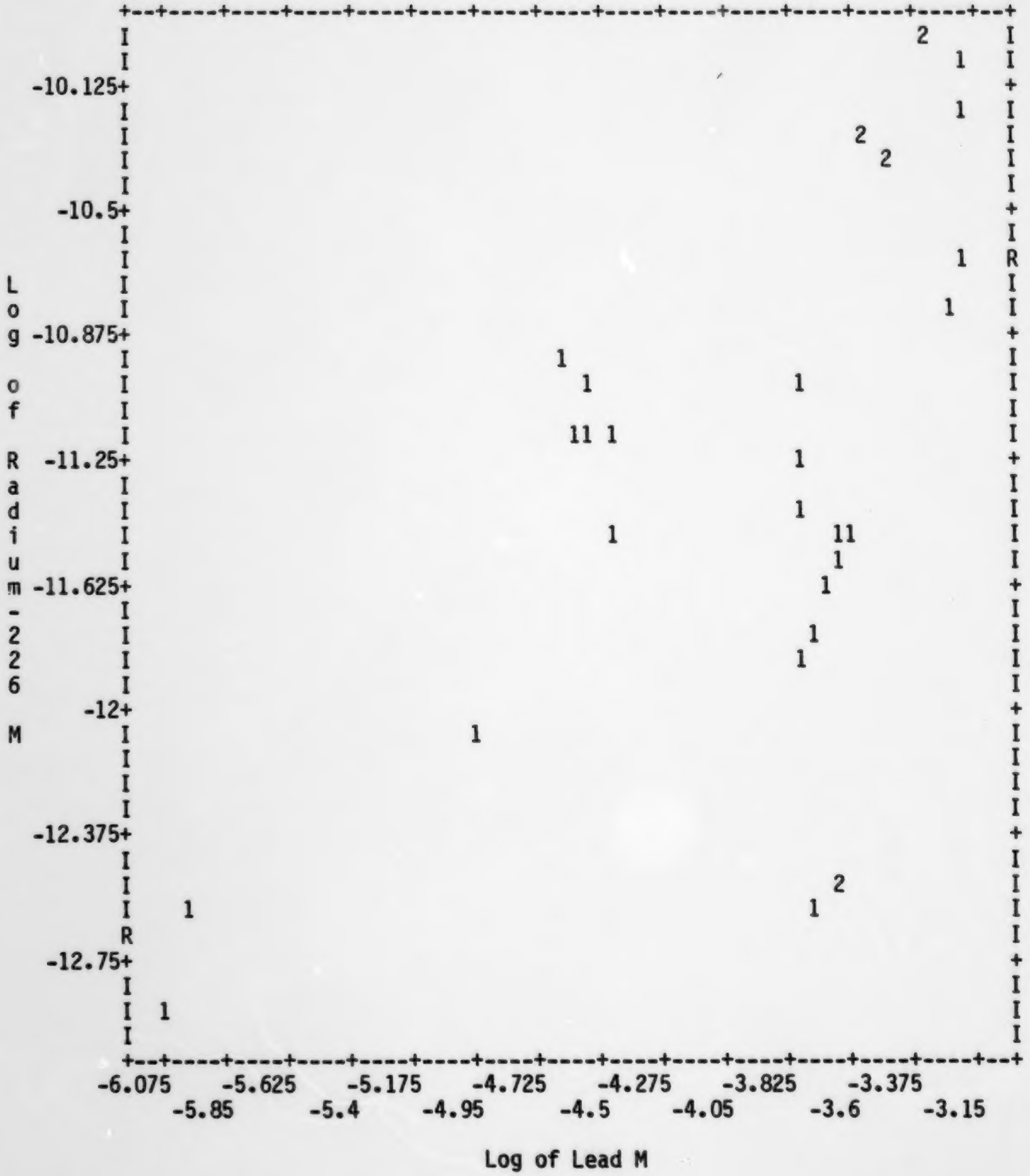
The correlation plots for Ra with Ba, and Ra with Pb (Fig. 9.4b; 9.5b; and Fig. 9.4e, 9.5e; respectively) show considerable scatter but the correlation coefficient is quite strong. The r^2 for the Ra-Ba plots is larger (r^2=0.77; 0.84 respectively) than that for the Ra-Pb plots (r^2=0.39; 0.41 respectively). The slope of the log-log relationships is somewhat closer to 1 for the Ra-Ba relationship than for the Ra-Pb relationship. A slope of 1 is expected if the mixed crystal density of Ra-226 in either $BaSO_4(s)$ or $PbSO_4(s)$ is uniform with depth in the crystal.

All standard errors of estimates given in the correlation plots have a level of significance described by 0.0000 (i.e., four zero's to the right of the decimal point). This means that the level of significance is greater than 0.00004. Note that a level of significance of 0.00004 indicates a stronger relationship statistically than a level of significance of 0.001. A level of significance commonly accepted for correlation analysis is 0.01 or 0.001. The calculated level of significance is a function of the degree of correlation divided by the number of data points. Hence, even if the variance explained by the correlation is low (i.e., r^2=0.1), the "level of significance" can be high if a large number of data points are used in the correlation. For this reason, the "level of significance" statistic is judged to be inadequate for interpretation of the degree of correlation in this study.

9.1(a) Correlation of Ra with Ba from all Acid Digestion Data

```
         ++----+----+----+----+----+----+----+----+----+----+----+----+----+----+
         I                                                                   11 R
         I                                                                 1    I
  -10.125+                                                                      +
         I                                                                  1   I
         I                                                 11                   I
         I                                                 2                    I
         I                                                                      I
    -10.5+                                                                      +
         I                                                                      I
         I                                                 1                    I
L        I                                                                      I
o        I                                              1                       I
g -10.875+                                                                      +
         I                                                1                     I
o        I                        1             1                               I
f        I                                                                      I
         I             1                    1       1                           I
R  -11.25+                                              1                       +
a        I                                                                      I
d        I                                      1                               I
i        I                          1       2                                   I
u        I                                      1                               I
m -11.625+                                      1                               +
-        I                                                                      I
2        I         1                                                            I
2        I 1                                                                    I
6        I                                                                      I
      -12+                                                                      +
M        I                 1                                                    I
         I                                                                      I
         I                                                                      I
         I                                                                      I
  -12.375+                                                                      +
         I                                                                      I
         I 2                                                                    I
         R             1            1                                           I
         I                                                                      I
   -12.75+                                                                      +
         I                                                                      I
         I                 1                                                    I
         I                                                                      I
         ++----+----+----+----+----+----+----+----+----+----+----+----+----+----+
              -7      -6.6      -6.2      -5.8      -5.4        -5      -4.6
       -7.2      -6.8      -6.4        -6      -5.6      -5.2      -4.8

                                     Log of Barium M

31 cases plotted. Regression statistics of RA on BA:
Correlation  .85698 R Squared  .73441  S.E. of Est     .44357 Sig.  .0000
Intercept(S.E.)   -5.87717(   .60490)  Slope(S.E.)      .92901(   .10374)
```

9.1(b) Correlation of Ra with Pb from all Acid Digestion Data



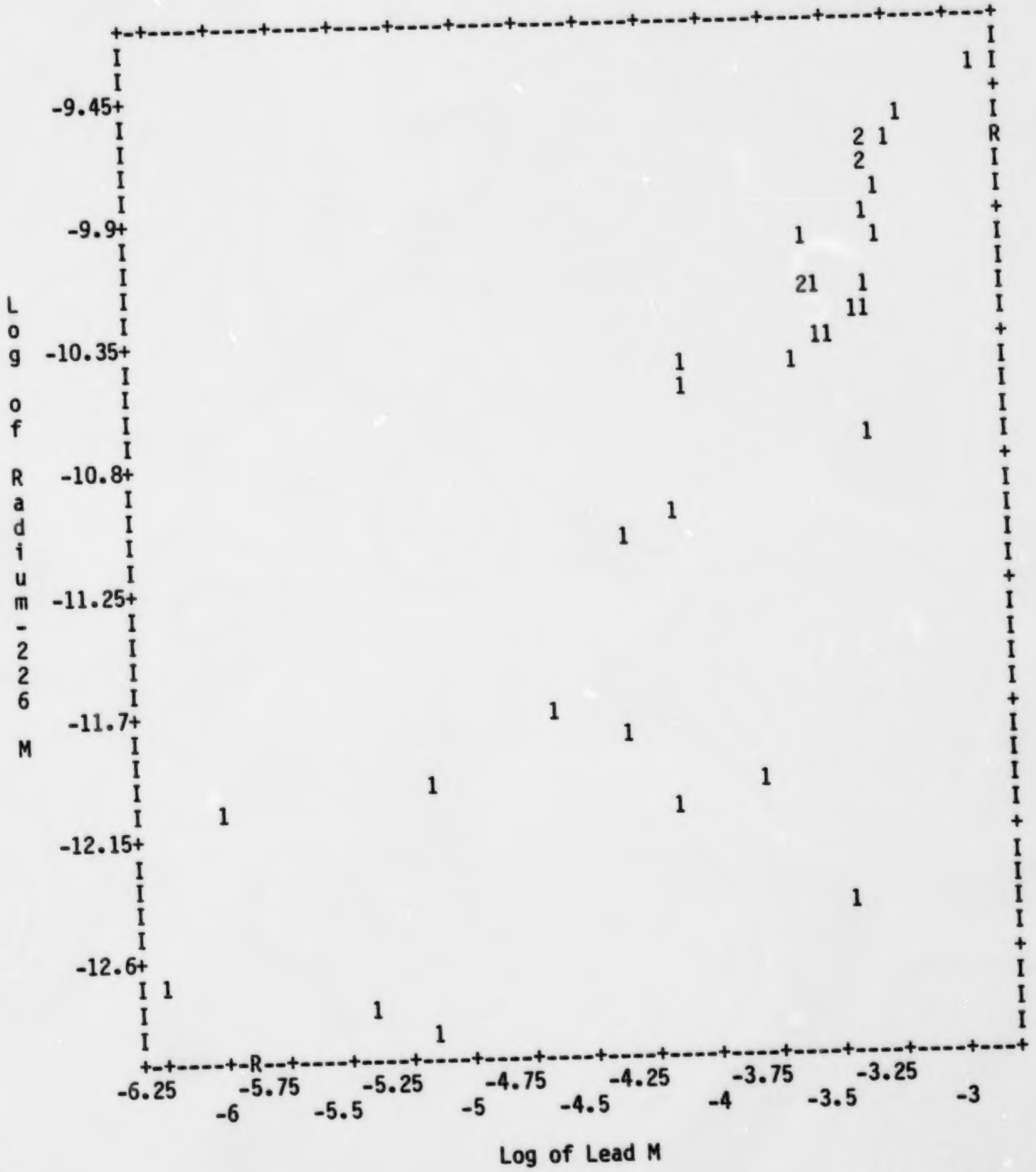
```
31 cases plotted. Regression statistics of RA on PB:
Correlation  .57087 R Squared  .32589  S.E. of Est     .70669 Sig.  .0008
Intercept(S.E.)   -8.66909(  .70006)  Slope(S.E.)     .65435(  .17476)
```

9.2(a)

Correlation of Ra with Ba from Leaching Pachucas Solids (EDTA Treatment)

```
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+-R+
          I                                                                      I
          I                                                                  1   I
     -9.45+                                                                      +
          I                                                                1     I
          I                                                          1  2        I
          I                                                             1   1    I
          I                                                           1          I
      -9.9+                                               1                      +
          I                                                      1       1       I
          I                                                                      I
 L        I                                          11    1 1                   I
 o        I                                        1                    1        I
 g  -10.35+                                       11                             +
          I                                        1       1                     I
 o        I                                                1                     I
 f        I                                                                      I
          I                                                        1             I
 R   -10.8+                                                                      +
 a        I                                                                      I
 d        I                                            1                         I
 i        I                    1                                                 I
 u        I                                                                      I
 m  -11.25+                                                                      +
 -        I                                                                      I
 2        I                                                                      I
 2        I                                                                      I
 6        I                                                                      I
     -11.7+                        1                                             +
 M        I                  1                                                   I
          I                                                                      I
          I             1        1                                               I
          I               1    1                                                 I
    -12.15+                                                                      +
          I                                                                      I
          I                                                                      I
          I             1                                                        I
          I                                                                      I
     -12.6+                                                                      +
          I  1                                                                   I
          I                     1                                                I
          R        1                                                             I
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
             -6.875    -6.325    -5.775    -5.225    -4.675    -4.125    -3.575
         -7.15      -6.6     -6.05      -5.5     -4.95      -4.4     -3.85

                                      Log of Barium M

35 cases plotted. Regression statistics of RA on BA:
Correlation  .93197 R Squared  .86857  S.E. of Est     .38915 Sig.  .0000
Intercept(S.E.)  -5.97639(   .32807)  Slope(S.E.)     .94641(   .06409)
```

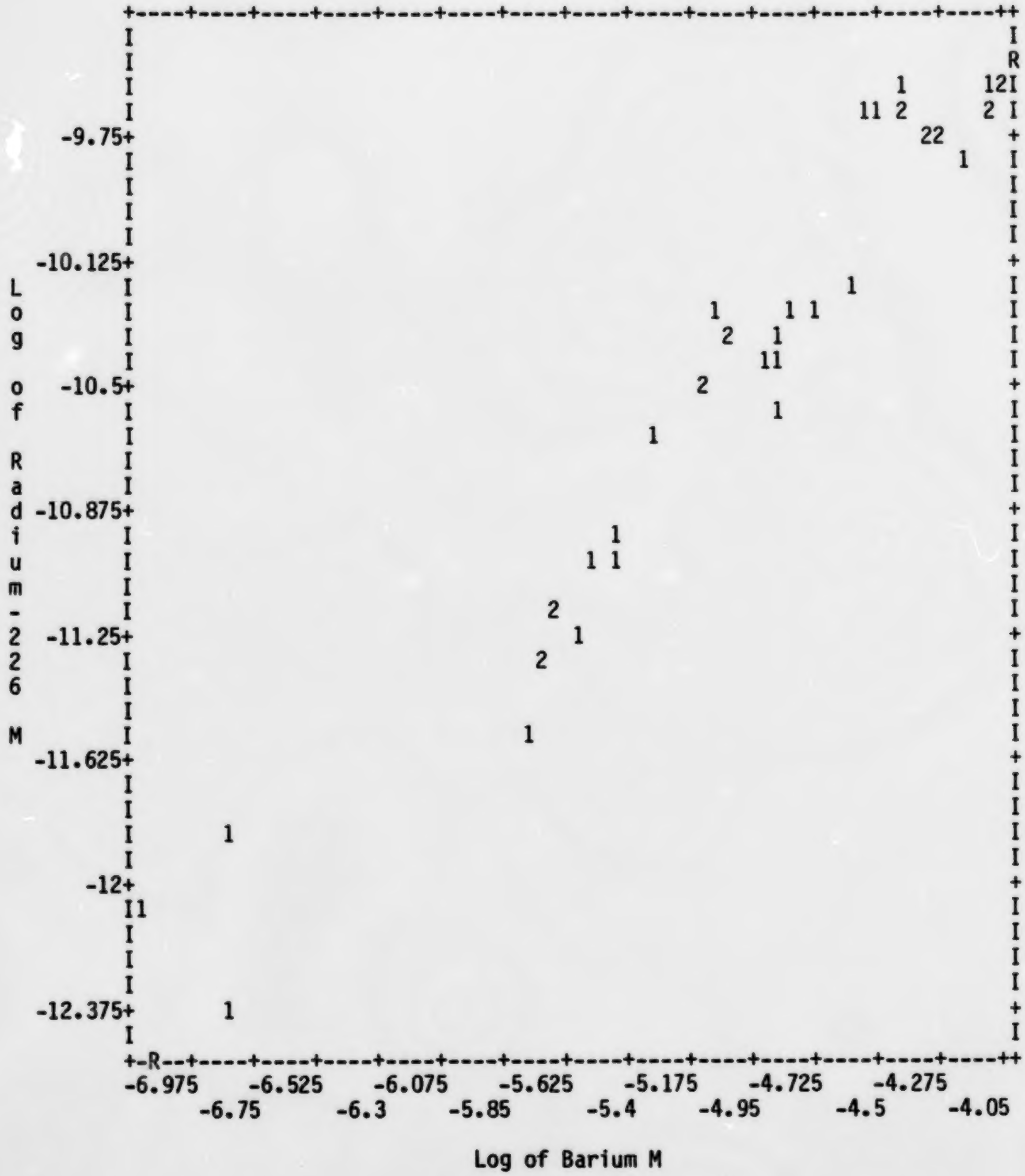
9.2(b) Correlation of Ra with Pb from Leaching Pachucas Solids
(EDTA Treatment)



```
35 cases plotted. Regression statistics of RA on PB:
Correlation  .82005 R Squared  .67248  S.E. of Est     .61431 Sig.  .0000
Intercept(S.E.)   -6.60960(   .51036)  Slope(S.E.)    1.05681(   .12839)
```

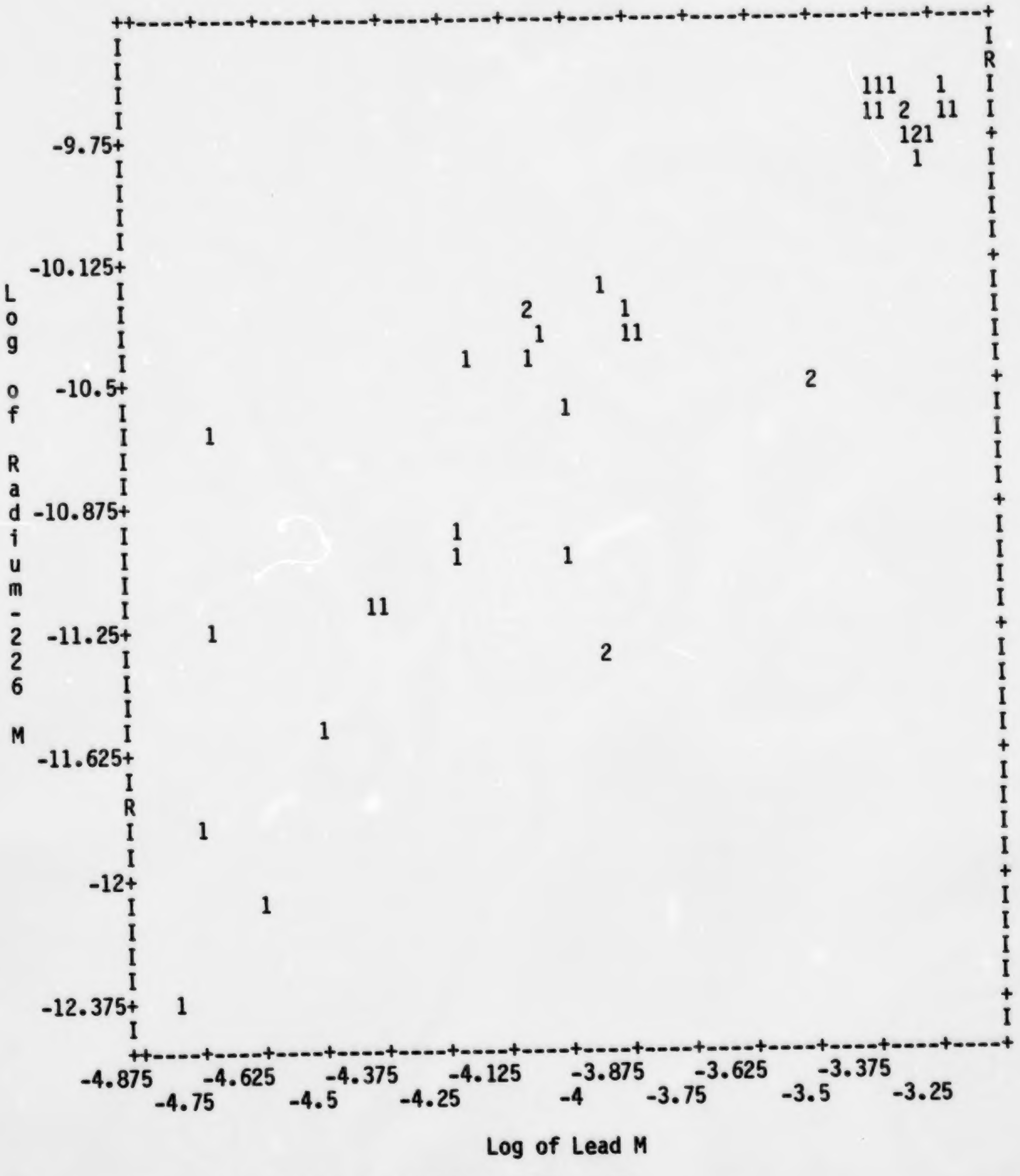
9.3(a)

Correlation of Ra with Ba from Leaching Pachucas Solids
(Salt and Acid Treatment)



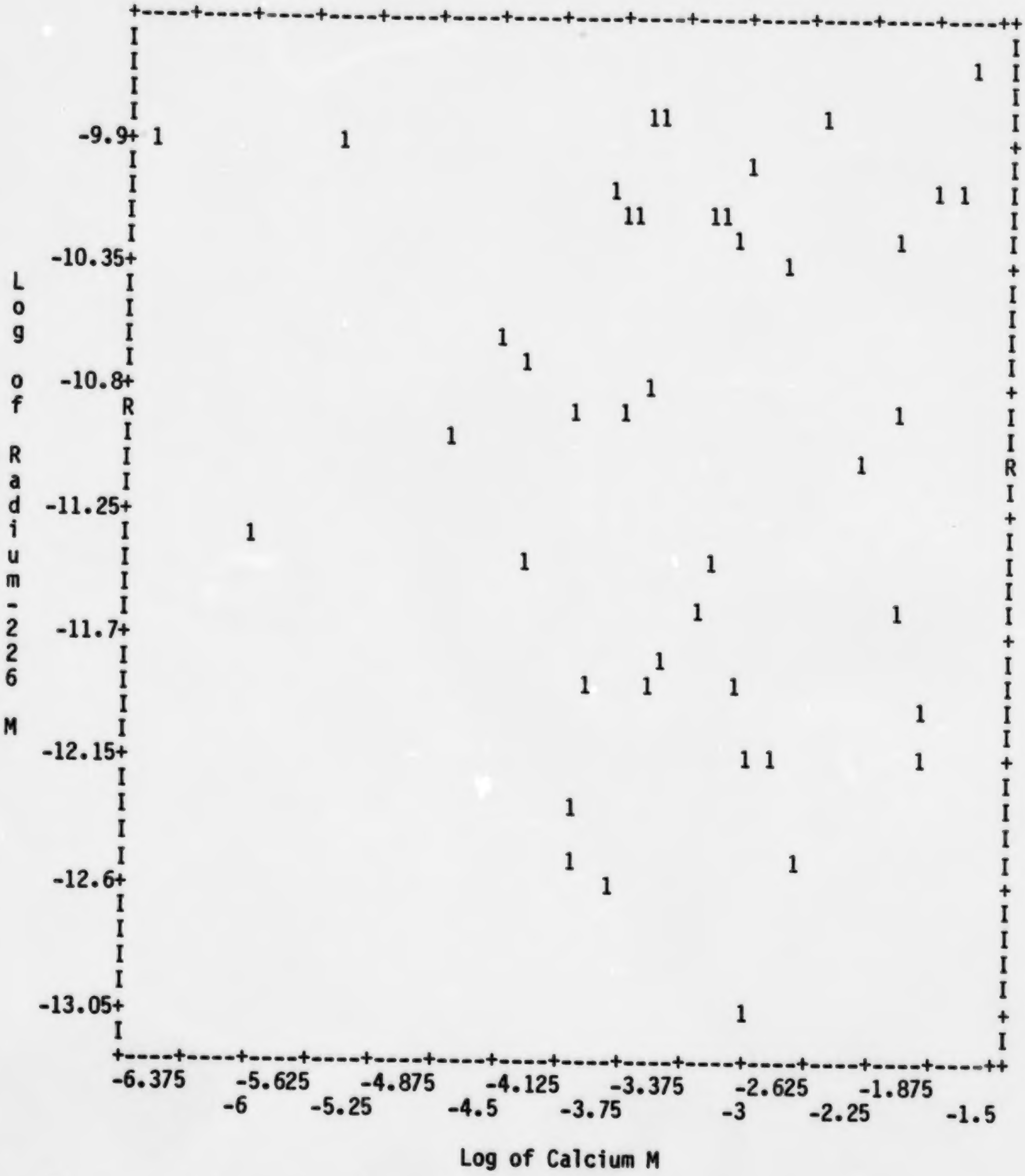
```
40 cases plotted. Regression statistics of RA on BA:
Correlation  .97154 R Squared  .94389  S.E. of Est     .18311 Sig.  .0000
Intercept(S.E.)   -5.67679(   .19051)  Slope(S.E.)     .95357(   .03771)
```

9.3(b) Correlation of Ra with Pb from Leaching Pachucas Solids
(Salt and Acid Treatment)



```
40 cases plotted. Regression statistics of RA on PB:
Correlation  .88289 R Squared  .77950  S.E. of Est     .36300 Sig.  .0000
Intercept(S.E.)   -5.44647(   .43444)  Slope(S.E.)    1.29994(   .11216)
```

9.4(a) Correlation of Ra with Ba from Tailings Solids

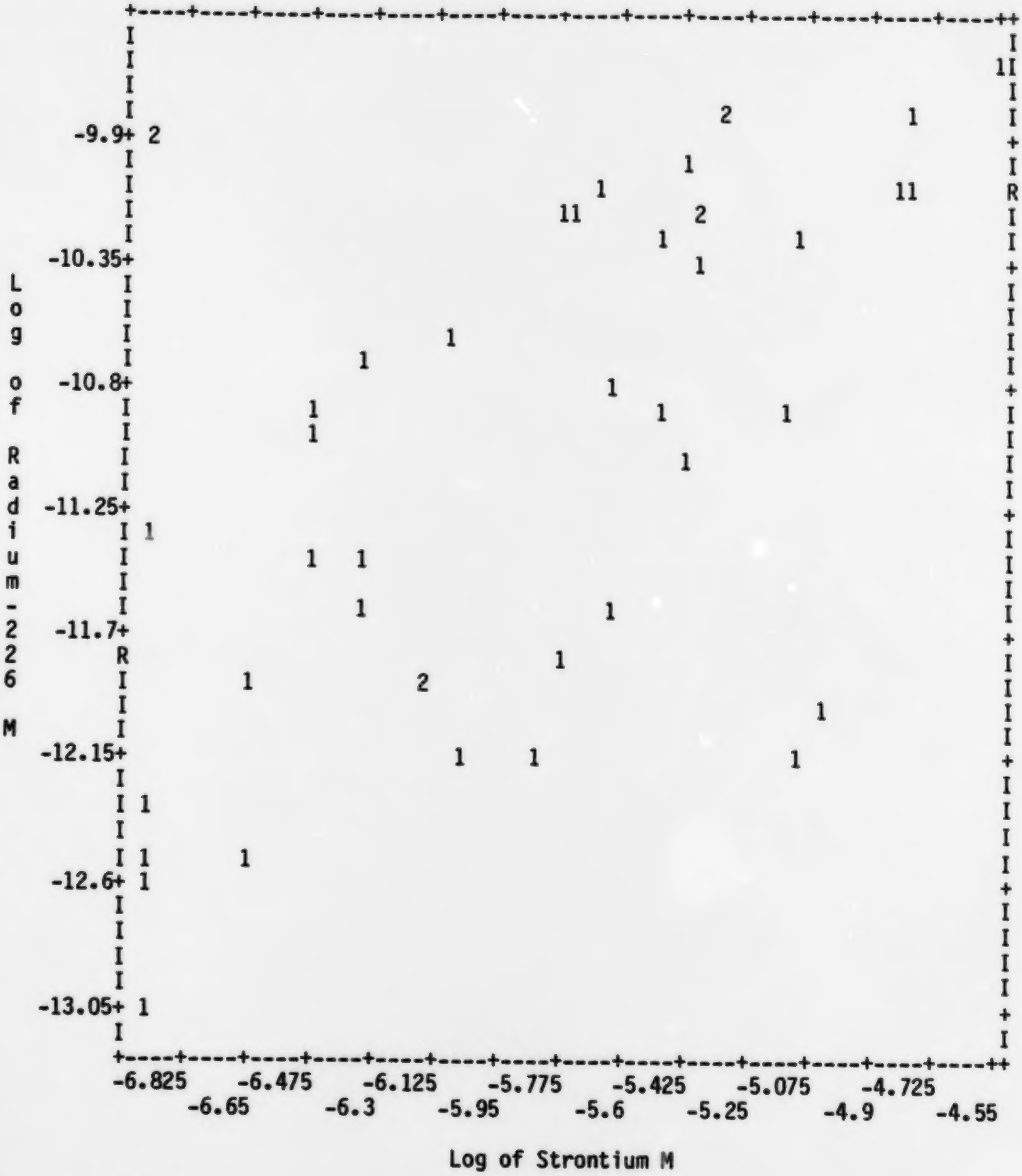


```
43 cases plotted. Regression statistics of RA on CA:
Correlation -.04118 R Squared  .00170  S.E. of Est     .97725 Sig.  .7932
Intercept(S.E.)  -11.14585(   .49121)  Slope(S.E.)    -.03650(   .13830)
```

9.4(b) Correlation of Ra with Ba from Tailings Solids

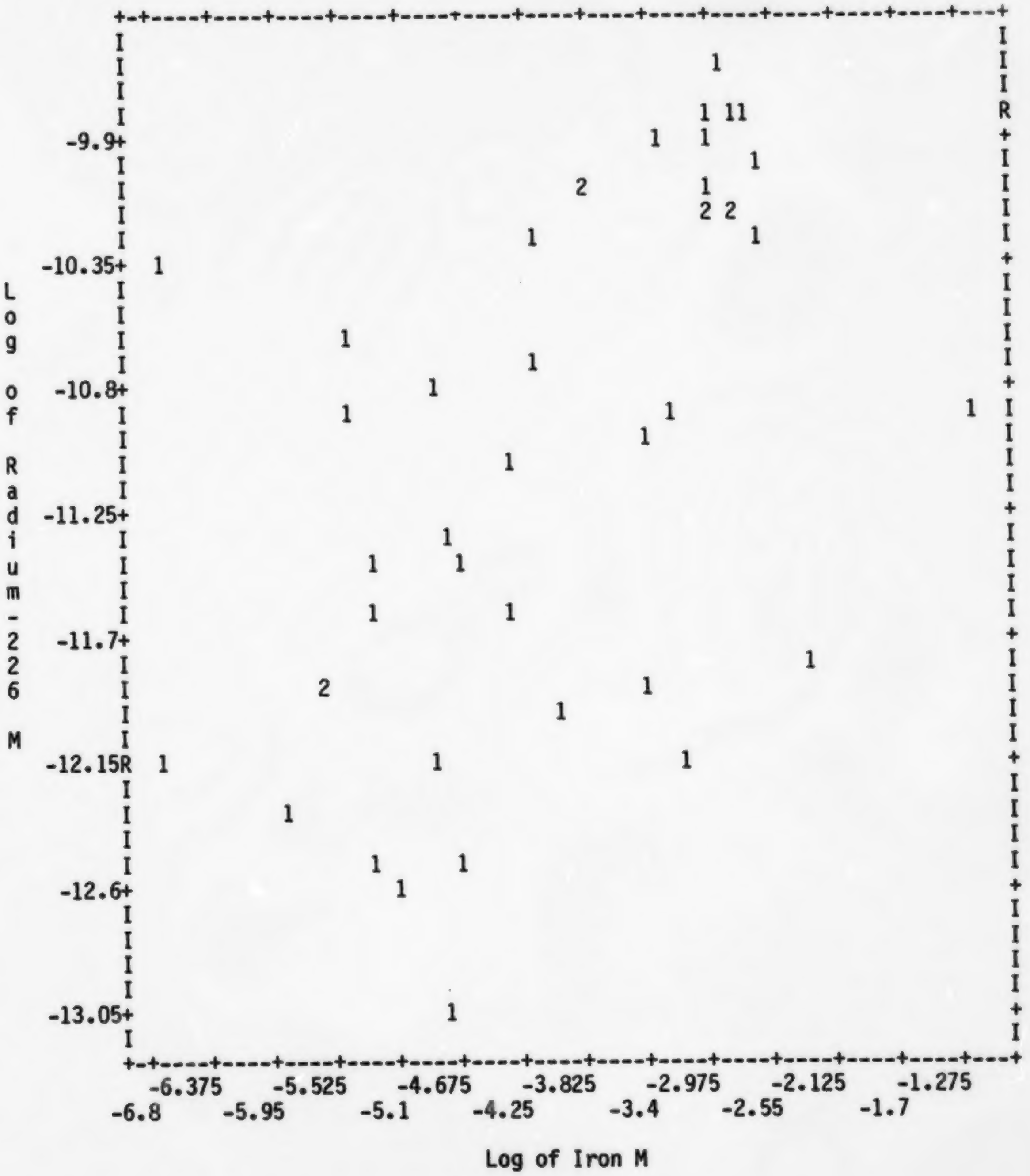
```
         +-+----+----+----+----+----+----+----+----+----+----+----+----+----+-R-+
         I                                                                      I
         I                                                                   1  I
         I                                                                      I
         I                                                  11              1   I
     -9.9+                                              11                      +
         I                                                            1         I
         I                                         1               1  1         I
         I                                               13                     I
         I                                                        1 1           I
   -10.35+                                                    1                 +
L        I                                                                      I
o        I                                                                      I
g        I                        1                                             I
         I                   1                                                  I
o   -10.8+                                            1                         +
f        I                         1 1                    1                     I
         I               1                                                      I
R        I                                               1                      I
a        I                                                                      I
d  -11.25+                                                                      +
i        I              1                                                       I
u        I       1           1                                                  I
m        I                                                                      I
-        I 1             1                                                      I
2   -11.7+                                                                      +
2        I 1                                                                    I
6        I 1               11                                                   I
         I                      1                                               I
M        I                                                                      I
   -12.15+ 1            1    1                                                  +
         R                                                                      I
         I              1                                                       I
         I                                                                      I
         I       1    1                                                         I
    -12.6+          1                                                           +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
   -13.05+ 1                                                                    +
         I                                                                      I
         +-+----+----+----+----+----+----+----+----+----+----+----+----+----+---+
           -6.875    -6.325    -5.775    -5.225    -4.675    -4.125    -3.575
       -7.15      -6.6     -6.05      -5.5     -4.95      -4.4     -3.85

                                     Log of Barium M

43 cases plotted. Regression statistics of RA on BA:
Correlation  .88017 R Squared  .77469  S.E. of Est     .46426 Sig.  .0000
Intercept(S.E.)   -6.99854(   .34621) Slope(S.E.)      .73350(   .06178)
```

9.4(c) Correlation of Ra with Sr from Tailings Solids



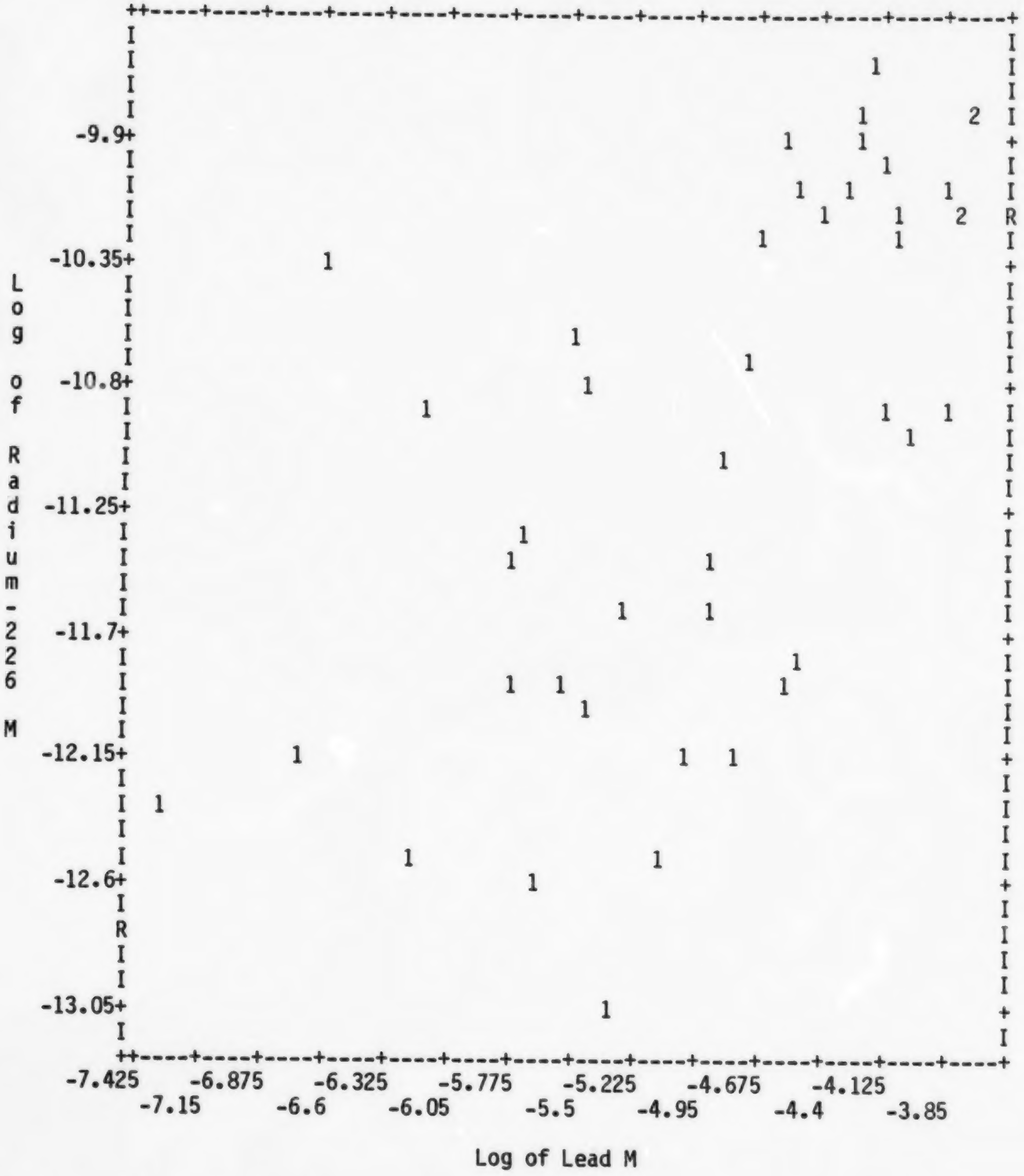
```
43 cases plotted. Regression statistics of RA on SR:
Correlation  .53808 R Squared  .28953  S.E. of Est     .82441 Sig.  .0002
Intercept(S.E.)   -6.68889( 1.06757) Slope(S.E.)     .73710(   .18033)
```

9.4(d) Correlation of Ra with Fe from Tailings Solids



```
43 cases plotted. Regression statistics of RA on FE:
Correlation  .53664 R Squared   .28798  S.E. of Est      .82531 Sig.  .0002
Intercept(S.E.)   -9.36841(   .42520)  Slope(S.E.)      .40917(   .10048)
```

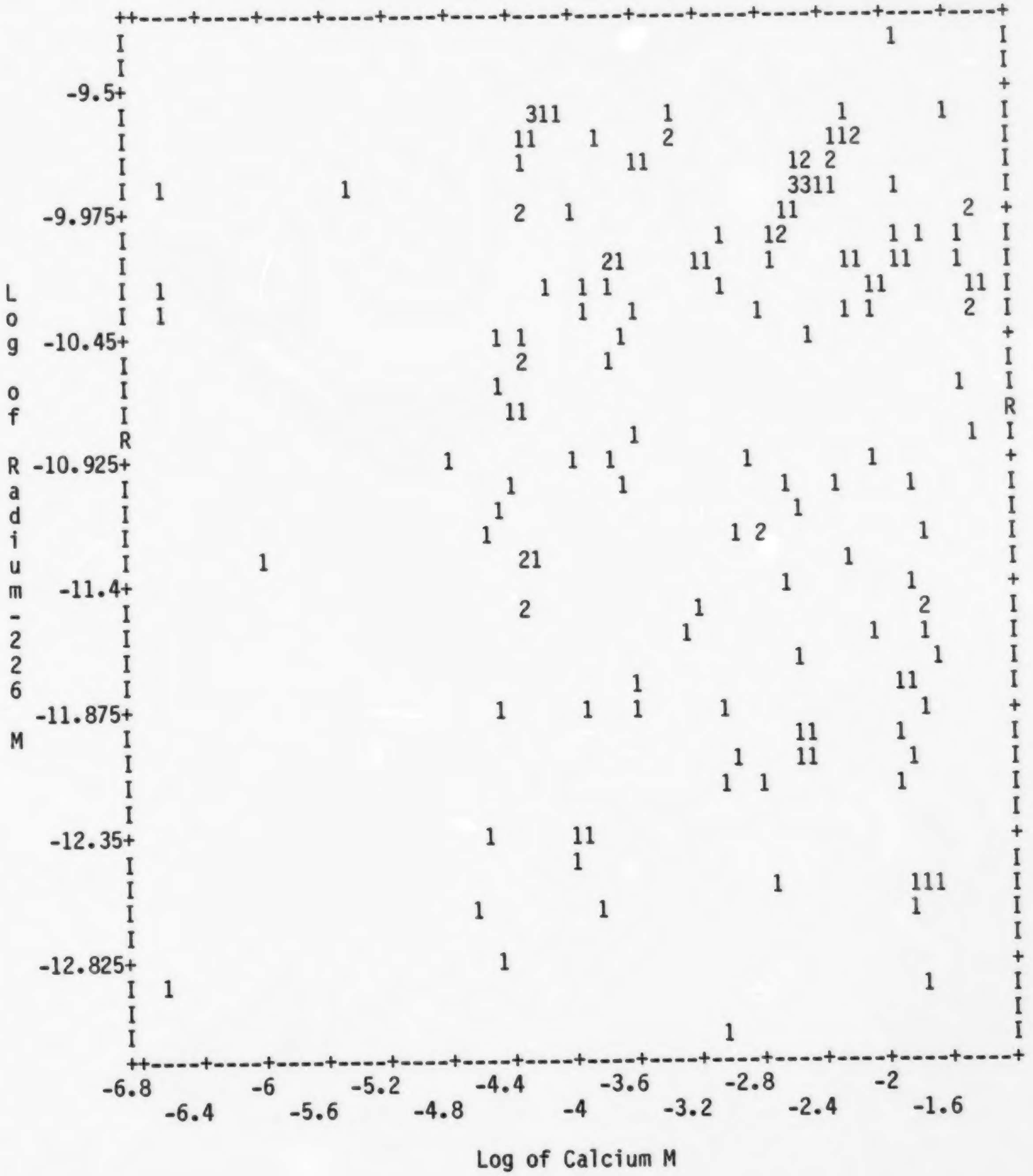
9.4(e) Correlation of Ra with Pb from Tailings Solids



```
43 cases plotted. Regression statistics of RA on PB:
Correlation  .62479 R Squared  .39036  S.E. of Est     .76368 Sig.  .0000
Intercept(S.E.)   -7.70507(   .65782)  Slope(S.E.)     .67928(   .13257)
```

9.5(a) Correlation of Ra with Ca for all Data

(except $CaCl_2$ extractant)



```
159 cases plotted. Regression statistics of RA on CA:
Correlation  .01508 R Squared  .00023  S.E. of Est     .95944 Sig.  .8504
Intercept(S.E.)  -10.73568(   .21415)  Slope(S.E.)     .01232(   .06522)
```

9.5(b) Correlation of Ra with Ba for all Data

(except $BaCl_2$ extractant)

```
         +-+----+----+----+----+----+----+----+----+----+----+----+----+----+----+R--+
         I                                                                 1    I
         I                                                                      I
     -9.5+                                                                      +
         I                                                   1    13 1   1   1  I
         I                                                11 2 1  11 2   1      I
         I                                                  1111 3 2        1   I
         I                                              21   1 23 1  1          I
   -9.975+                                                 2  11       1        +
         I                                                1    21  1  2         I
         I                                         21    241    1               I
L        I                                    1111   1 1  1       1 1 1         I
o        I                                    2 112 11        1                 I
g  -10.45+                                      11   1   2                      +
         I                                      1    1                          I
o        I                        1          11                                 I
f        I                   1                                   1              I
         I                                 1          1                         I
R -10.925+               1         1 1    1  1            1                     +
a        I                  1         1 1 1           1  1                      I
d        I                   1        1                                         I
i        I          1              1  1  1 1                                    I
u        I              1            2  1                                       I
m   -11.4+                         1  1                                         +
-        I       1           2     1 1                                          I
2        I 1             1            1                                         I
2        I                       1    1                                         I
6        I 1     1         1                                                    I
  -11.875+ 2     1         11                                                   +
M        I            1        11                                               I
         I 1          1 1    1                                                  I
         I 1            1    1                                                  I
         I                                                                      I
   -12.35+       1    1 1                                                       +
         R            1                                                         I
         I 2     1  1                                                           I
         I 1        1        1                                                  I
         I                                                                      I
  -12.825+                    1                                                 +
         I       1    1                                                         I
         I                                                                      I
         I 1                                                                    I
         +-+----+----+----+----+----+----+----+----+----+----+----+----+----+---+
           -6.875    -6.325    -5.775    -5.225    -4.675    -4.125    -3.575
       -7.15      -6.6     -6.05      -5.5     -4.95      -4.4     -3.85

                                     Log of Barium M
```

```
164 cases plotted. Regression statistics of RA on BA:
Correlation  .91542 R Squared  .83800  S.E. of Est      .38301 Sig.  .0000
Intercept(S.E.)  -6.28499(  .15736) Slope(S.E.)      .85919(   .02968)
```

9.5(c)

Correlation of Ra with Sr for all Data

```
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
         I                                             1                        I
         I                                                                      I
     -9.5+                                                                      +
         I                              1    3111       1                       I
         I                              1   221  12                         1   I
         I                                2  3 11   1            1          1   R
         I   2                              4211    1                           I
   -9.975+                                1 11      11                          +
         I                               13        111                          I
         I                        111    211  11  1  1                          I
L        I                     1    2  1     12  1 1                         1  I
o        I   1                 1    1    1 1 1     3                            I
g  -10.45+                    1 1            1      1                        1  +
         I                                          1            1              I
o        I                  1       1               1                           I
f        I              1                   1                                   I
         I                          1               1                           I
R -10.925+           2      1      1   1     1                                  +
a        I                 1      1     2   1            1                      I
d        I                      1    1                                          I
i        I                  1  1        2                  1                    I
u        I   1                  1    2                                          I
m   -11.4+                                1               1                     +
-        I           1  1         1                        2                    I
2        R              1            1                     1                    I
2        I                          1                      1                    I
6        I                        1           1           1                     I
  -11.875+        1        21                             1                     +
M        I                           2         1                                I
         I               1          1  1             1                          I
         I                   1  1             1                                 I
         I                                                                      I
   -12.35+   1    1         1                                                   +
         I   1                                                                  I
         I        1                      1                11                    I
         I   1                  1                        1                      I
         I                                                                      I
  -12.825+                    1                                                 +
         I        1                           1                                 I
         I                                                                      I
         I   1                                                                  I
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
        -6.875    -6.325    -5.775    -5.225    -4.675    -4.125    -3.575
               -6.6     -6.05      -5.5     -4.95      -4.4     -3.85      -3.3

                                   Log of Strontium M
```

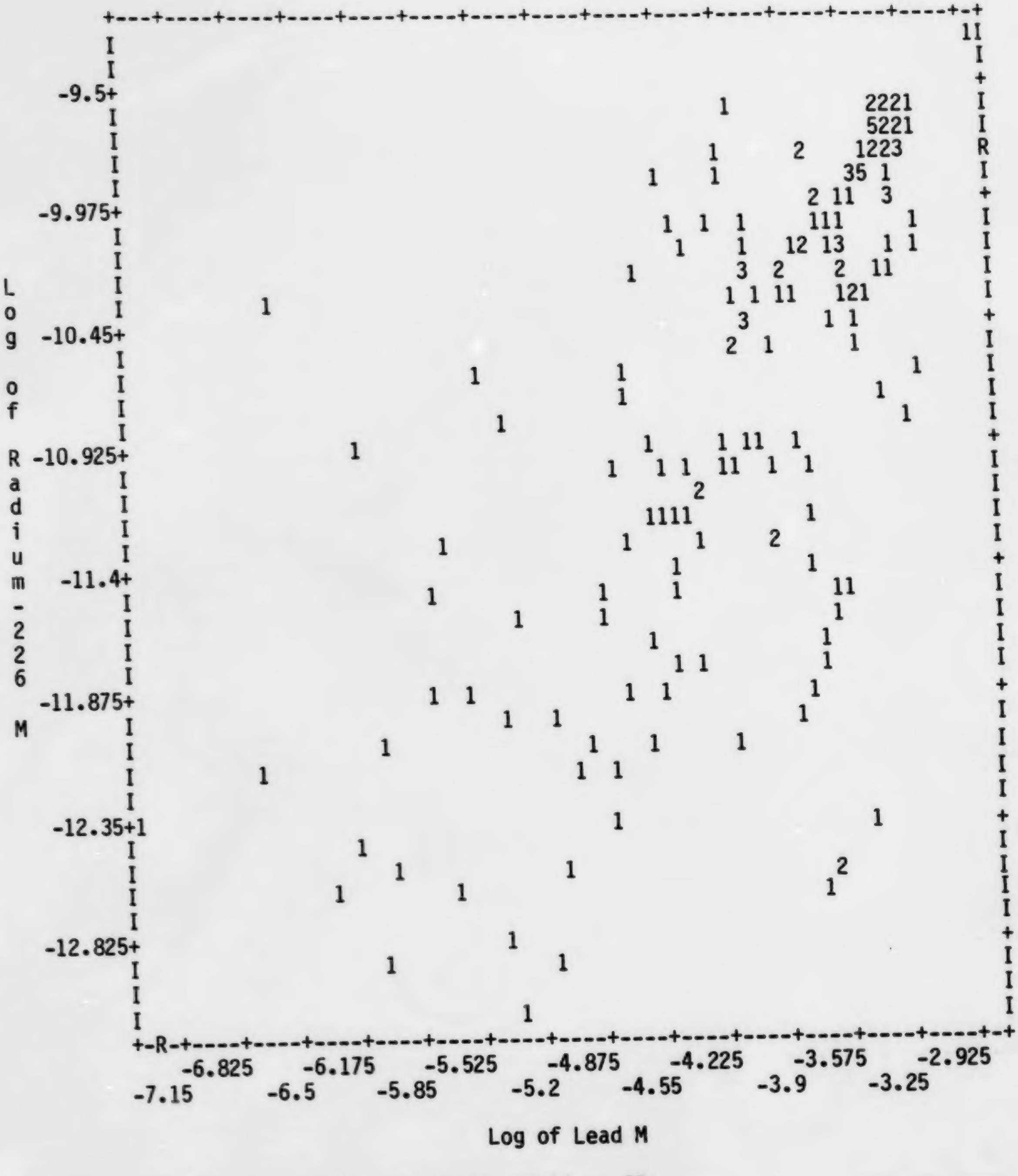
```
164 cases plotted. Regression statistics of RA on SR:
Correlation  .36526 R Squared  .13341  S.E. of Est     .88585 Sig.  .0000
Intercept(S.E.)   -8.14818(   .52699) Slope(S.E.)     .48631(   .09738)
```

9.5(d)

Correlation of Ra with Fe for all Data (except $FeCl_3$ extractant)

```
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
         I                                           1                          I
         I                                                                      I
     -9.5+                                                                      +
         I                              12      21    1                         I
         I                     11       2       22                              I
         I                              21     13 21    1                       I
         I                                   1153               1               I
   -9.975+                            11      12            2                   +
         I                              1     2 1  11                 1         I
         I                              1    11 2 2      1       1  1 1         R
L        I        1      1       1  1         1     1     11       1            I
o        I 1      1              1                         2     11           1 I
g  -10.45+                         1     21  1                                  +
         I                      1    2   1                                      I
o        I              1    1                                        1         I
f        I                          1        1                                  I
         I                   1                                        1         I
R -10.925+             1             1      11  1                1              +
a        I                         1111              1     1       1            I
d        I                      1   1                                           I
i        I                          1                  1   1 1     1            I
u        R                    1     1 12                                        I
m   -11.4+                                                  1      1            +
-        I               1     1    1                              2            I
2        I                1        1                               1            I
2        I               1                                         1            I
6        I                                             1  1        1            I
  -11.875+            2                  1  1                    1              +
M        I              1             1  1                                      I
         I          1    1                     1     1                          I
         I 1                  1                1                                I
         I                                                                      I
   -12.35+         1                      1 1                                   +
         I               1                                                      I
         I            1        1                                  11            I
         I 1               1                                      1             I
         I                                                                      I
  -12.825+                  1                                                   +
         I        1                  1                                          I
         I                                                                      I
         I                     1                                                I
         +---+----+----+----+----+----+----+----+----+----+----+----+----+----+-+
          -6.5      -5.5      -4.5      -3.5      -2.5      -1.5       -.5
                 -6        -5        -4        -3        -2        -1         0

                                      Log of Iron M

166 cases plotted. Regression statistics of RA on FE:
Correlation  .24598 R Squared  .06050  S.E. of Est     .91250 Sig.  .0014
Intercept(S.E.)  -10.22579(  .18155) Slope(S.E.)     .16291(  .05013)
```

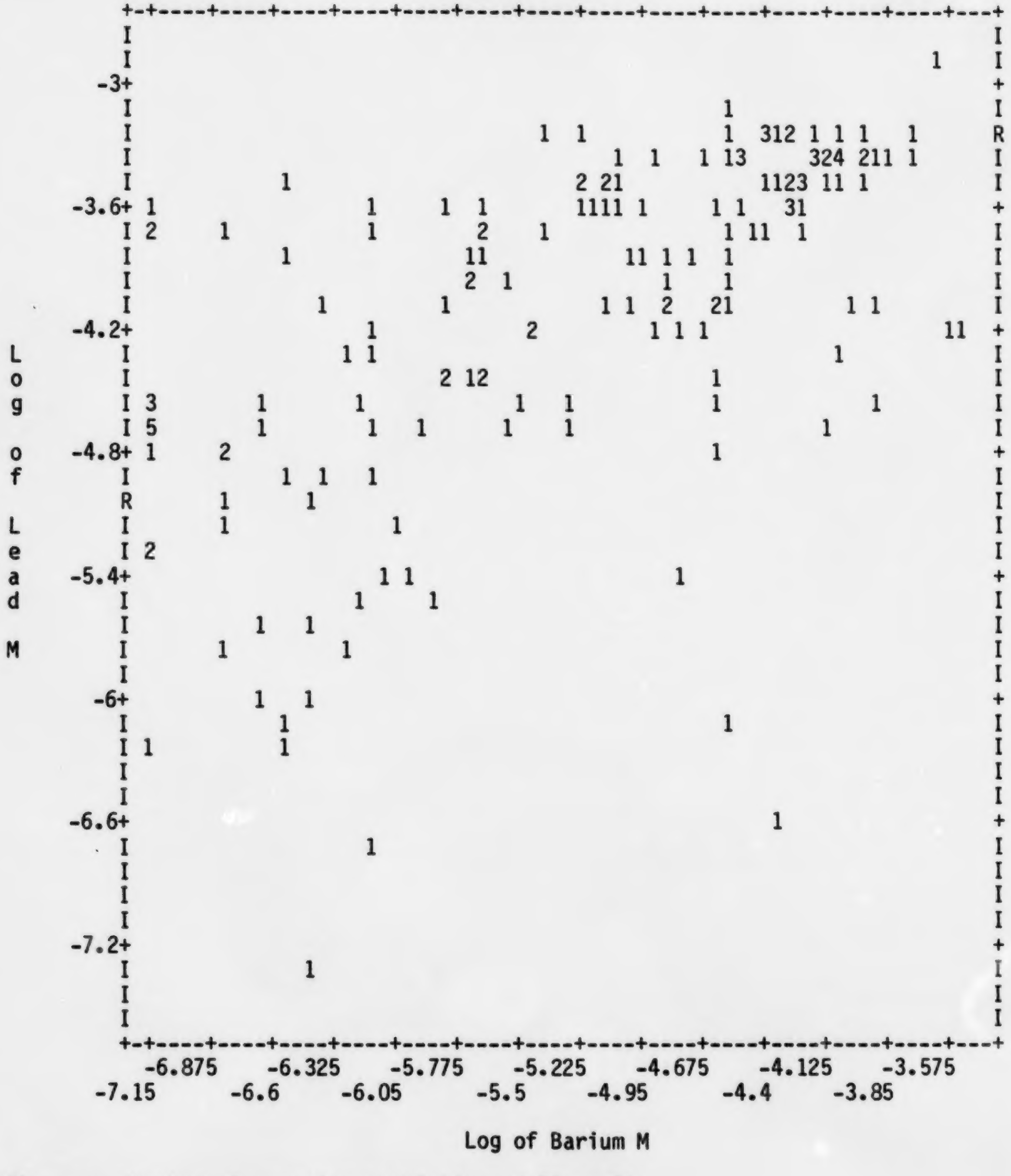
9.5(e) Correlation of Ra with Pb for all Data



```
171 cases plotted. Regression statistics of RA on PB:
Correlation  .67229 R Squared  .45197  S.E. of Est     .69597 Sig.  .0000
Intercept(S.E.)   -7.67277(   .26556)  Slope(S.E.)      .74783(   .06334)
```

9.5(f)

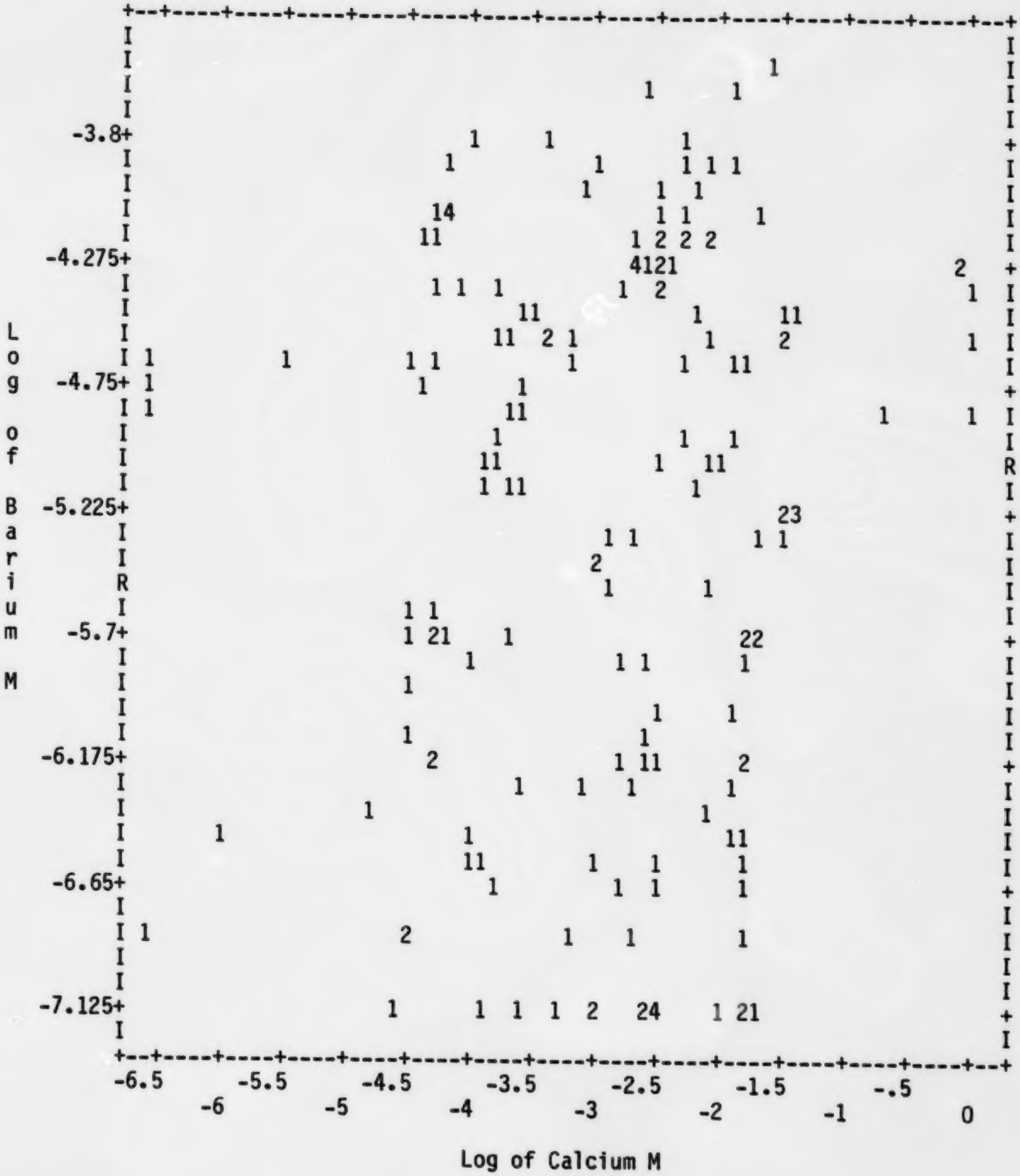
Correlation of Pb with Ba for all Data
(except $BaCl_2$ extractant)



```
170 cases plotted. Regression statistics of PB on BA:
Correlation  .58509 R Squared  .34233  S.E. of Est     .68903 Sig.  .0000
Intercept(S.E.)   -1.64709(  .27101)  Slope(S.E.)     .47160(  .05043)
```

9.5(g)

Correlation of Ba with Ca for all Data (except $BaCl_2$ extractant)



```
171 cases plotted. Regression statistics of BA on CA:
Correlation  .07645 R Squared  .00584  S.E. of Est    1.05762 Sig.  .3203
Intercept(S.E.)   -5.09181(  .20691)  Slope(S.E.)      .06524(   .06546)
```

9.5(h) Correlation of Sr with Ca for all Data

```
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
          I                                                                 22   I
          I                                                                      I
      -3.6+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
     -4.05+                                                            1      2  R
          I                                                                      I
          I                                                                      I
          I                                                                      I
 L        I                                                 44                   I
 o    -4.5+                                                 4 1                  +
 g        I                                                1                     I
          I                                                    2                 I
 o        I                             11         2     1 11 31                 I
 f        I                            1                12 1    3                I
     -4.95+                                            21      1                 +
 S        I                                 1          1   3                     I
 t        I                        23 1     1        412 2122                    I
 r        I                       122   1   1        5   2                       I
 o        I                               11       511 11                        I
 n    -5.4+                             11      1 1 13 1    1                    +
 t        I                        1 1   1     1  212                            I
 i        I                        11               12                           I
 u        I                            1112        1 2                           I
 m        I                        3      1   2 2      1                         I
     -5.85+                        1            1                                +
 M        I 1                    12 1    11                                      I
          I                      2                1                              I
          I                      31       1    1 2                               I
          I                                     1                                I
      -6.3+                        2         1                                   +
          I                                                                      I
          I                   1       1       1                                  I
          I                                                                      I
          I 1                           2           1                            I
     -6.75+                                                                      +
          I                                                                      I
          R 2     1    1              2 1       1                                I
          I                                                                      I
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
          -6.5      -5.5      -4.5      -3.5      -2.5      -1.5       -.5
                 -6        -5        -4        -3        -2        -1        0

                                      Log of Calcium M

177 cases plotted. Regression statistics of SR on CA:
Correlation  .76326 R Squared  .58257  S.E. of Est     .45209 Sig.  .0000
Intercept(S.E.)   -4.12039(   .08644)  Slope(S.E.)     .42389(   .02712)
```

The question of an acceptable correlation coefficient (r; or coefficient of determination, r^2) is open to judgement. r^2 represents the portion of the total variation explained by the correlation line. Different professional fields use different values (r^2=0.5; or 0.8) depending upon the nature of the data. The definition of r^2 and a discussion of a useful rule of thumb for the interpretation of r^2 are given in Appendix 3.

A crude "rule of thumb" suggested by Colton (1974) is judged to provide a useful perspective for this study. It is: "values of r^2 between 0 and 0.13 indicate little or no relationship; those between 0.25 and 0.56 indicate a moderate relationship, and those above 0.56 indicate a good-to-excellent relationship. For this rule of thumb, both the Ra-Ba and Ra-Pb correlations in each experiment and for all data (Fig. 9.5) are judged as acceptably strong correlations. But the statistics do not allow one to determine that one or the other correlation is more significant. More consistency is observed for the Ra-Ba correlation in individual experiments, but the results do not allow an unambiguous conclusion to be made.

Another statistical technique for determining whether barium or lead better explain Ra-226 dissolution is the use of multiple regression analysis. Multiple regression is a method for asking the question: If barium or lead are viewed as competitive variables, which one best explains the Ra data. If one consistently better explains the data, does the other one make a substantive (or significant) additional contribution to explaining the residual variance of Ra-226 data after the first variable is accounted for.

The results of using a backwards technique of multiple elimination regression for regressing Ra on Ba and Pb are given in Table 9.1 for all experiments. The initial line obtained in the regression is given in the third column, the final line obtained by backward elimination is given in the fourth column. In 3 cases (#7, 12, 13), the initial regression line is not modified by backwards elimination. The last column gives the significance of the T statistic used to eliminate a variable if one variable is eliminated from the initial regression line, or it gives the significance for the variable which would be eliminated if a stricter elimination criteria is used. In this report, a level of significance of 5% is used as the elimination criteria. The bracketted symbol in the last column is the variable (Ba or Pb) described by the significance statistic.

TABLE 9.1

MULTIPLE LINEAR REGRESSION ANALYSIS OF DATA FROM ACID DIGESTION

No.	Description	Initial Regression Line	Final Regression Line	Significance of Variable Eliminated
1.	Acid Digestion (Fig. 5.1)	LogRa = .318 LogBa + .659 LogPb - 6.45 ($r^2 = .905$)	LogRa = .877 LogPb - 7.33 ($r^2 = .884$)	(Ba) = .080
2.	Leaching Pachucas (Fig. 5.2)	LogRa = .52 LogBa - 1.31 LogPb - 13.39 ($r^2 = .533$)	LogRa = .546 LogBa - 8.39 ($r^2 - .506$)	(Pb) = .49
3.	EDTA on LP (Fig. 6.1)	LogRa = .774 LogBa - .306 LogPb - 5.59 ($r^2 - .956$)	LogRa = .918 LogBa - 6.03 ($r^2 - .947$)	(Pb) = .119
4.	EDTA on Well-Washed LP (Fig. 6.2)	LogRa = .906 LogBa = .033 LogPb - 6.42 ($r^2 = .925$)	LogRa = .927 LogBa - 6.46 ($r^2 = .924$)	(Pb) = .866
5.	Salt wash of LP (Fig. 6.3)	LogRa = .730 LogBa + .302 LogPb - 5.56 ($r^2 = .940$)	-	(Pb) = .0064
6.	Acid was of LP (Fig. 6.4)	LogRa = LogBa + .249 LogPb - 5.52 ($r^2 = .974$)	LogRa = .951 LogBa - 5.80	(Pb) = .31
7.	Salt/Acid wash of LP (Fig. 6.3, 6.4 = Fig. 9.3)	LogRa = .778 LogBa + .309 LogPb - 5.36 ($r^2 = .956$)	-	(Pb) = .003
8.	EDTA on Gunnar (Fig. 6.6)	LogRa = .877 LogBa + .023 LogPb - 6.56 ($r^2 = .983$)	LogRa = .883 LogBa - 6.66 ($r^2 = .983$)	(Pb) = .64
9.	EDTA on Lac Nor (Fig. 6.7)	LogRa = .714 LogBa - .013 LogPb - 6.77 ($r^2 = .893$)	LogRa = .710 LogBa - 6.75 ($r^2 = .892$)	(Pb) = .939
10.	Acid Digestion and Leaching (Fig. 5.1, 5.2 = Fig. 9.1)	LogRa = .821 LogBa + .24 LogPb - 5.56 ($r^2 = .768$)	LogRa = .929 LogBa - 5.88 ($r^2 = .734$)	(Pb) = .0527

TABLE 9.1 (con'd) MULTIPLE LINEAR REGRESSION ANALYSIS OF DATA FROM ACID DIGESTION

No.	Description	Initial Regression Line	Final Regression Line	Significance of Variable Eliminated
11.	EDTA on LP (Fig. 6.1, 6.2 = Fig. 9.2)	LogRa = .807 LogBa + .24 LogPb - 5.83 (r^2 = .911)	LogRa = .941 LogBa - 6.10 (r^2 = .900)	(Pb) = .105
12.	All Tailings Solids (Fig. 6.6, 6.7 + Misc. = Fig. 9.4)	LogRa = .625 LogBa + .321 LogPb - 6.02 (r^2 = .845)	-	(Pb) = .0001
13.	All Data (Fig. 9.5)	LogRa = .747 LogBa + . 229 LogPb - 5.92 (r^2 = .867)	-	(Pb) = .0000
14.	Adsorption Blanks (Fig. 8.1)	LogRa = .419 LogBa + .402 LogPb - 7.05 (r^2 = .82)	Pb is marginally better than Ba	(Ba) = .014 (Pb) = .011

The results of Table 9.1 indicate the following:

(i) For all single experiments except one (laboratory acid digestion), barium explains the variance of Ra-226 better than Pb does. This results from the higher value of r^2 for Ra-Ba than for Ra-Pb correlations (see Table 6.4).

(ii) In the single experiments, lead generally does not make an additional substantial contribution to explaining the residual variance of the Ra-Ba linear regression. When it is included in the regression before backwards elimination (see Col. 3, Table 9.1), the effect of Pb is additive in a few cases and negative in the others.

(iii) In data sets formed from combining single data sets, barium alone explains most of the variance (i.e., Pb is not significant) in two combined data sets (#10 Table 9.1 acid digestion plus leaching liquor data; #11 Table 9.1 EDTA on LP solids) while Pb also makes a "statistically significant" contribution for three combined data sets (#7, 12, 13; Table 5.11). However, in these three combined data sets, the increase in r^2 caused by including Pb in the regression is small compared to excluding it (e.g., with the inclusion of Pb, r^2 increases from .944 to .956 for #7; from .775 to .845 for #12; and from .838 to .867 for #13).

(iv) The regression relationship between Ra-226 dissolved and Ba dissolved is essentially the same using EDTA extraction of two different leaching pachuca solids samples (December 1984: #3 in Table 9.1; February 1985: well washed LP solids - #4 in Table 9.1). This suggests that the leaching process is consistent from month to month on essentially the same ore.

(v) The relationship between Ra-226 and Ba dissolved in the combined EDTA data set (#11, Table 9.1) and in the combined laboratory digestion/leaching liquor data set (#10, Table 9.1) is essentially the same. This supports the hypothesis that leaching solution concentrations and the solid concentration of Ra-226 in a host sulphate crystal on the leaching pachuca solids can be explained by a coprecipitation mechanism.

(iv) The regression relationships obtained for all data sets are quite similar, particularly when more than one data set is used in the regression. But the coefficient of determination (r^2) decreases when more data sets are added to the regression, reflecting the point that different tailings do have somewhat different relationships.

Further Required Experimental Work

The multiple regression analysis suggests that barium better explains the Ra-226 dissolution data than does lead. But the results of such statistical techniques do not prove cause-effect. Accordingly, we need to use other concepts, and theory, and further experimentation to determine whether both cations (Ba, Pb) or one main cation controls Ra-226 behaviour. This can be carried out using other extraction agents which have a greater chemical selectivity for one metal compared to the other. We have recently identified such an agent, but were unable to obtain it before the conclusion of this contract. A most high powered approach is use of distilled water or a water of low ionic strength (see recommendations).

It is improbable that a combined (Pb, Ba)SO_4 coprecipitate would control Ra-226 because the correlations between Pb and Ba for all the data (Fig. 9.5) and for individual experiments are too low. But the question of mixed crystal formation cannot, a priori, be disregarded because of the evidence for strontium affecting the capture of radium by other metal sulphates (see appendix) and the data of this report indicating capture of cations by gypsum formed in leaching pachuca liquor. More theoretical work (thermodynamical evaluation of mixed crystal formation; and kinetics of coprecipitation) and experimental work are required to resolve the potential influences of other mixed crystals on Ra-226 dissolution.

Regression of Analysis of Adsorption Data

Correlation analysis of Ra-226, Ba and Pb in the blanks of the adsorption experiment have been presented in Figures 8.1a, b. The correlation of Ra-226 with Ba(r^2=.798) is essentially the same as Ra-226 with Pb(r^2=.809). Multiple regression analysis gives the equation given in Table 9.1 involving Ra regressed upon Ba and Pb. Backward elimination gives Pb as the significant variable after elimination of Ba; the actual regression equation is not given in Table 9.1 because the difference between eliminating either Ba or Pb from the initial regression equation is not substantial (see Table 9.1 - "significance of variable eliminated" column).

These relationships also suggest that Ra-226 behaviour is controlled by its coprecipitation with $BaSO_4(s)$ and/or $PbSO_4(s)$. This provides further evidence for the postulate that K_D values obtained in sulphuric acid solutions are caused by Ra-226 coprecipitation with barite or anglesite.

10.0 SURFACE STUDIES

Studies using Secondary Ion Mass Spectrometry (SIMS), X-ray Photoelectron Spectroscopy (XPS also called ESCA), Auger Spectroscopy, Mossbauer, and Scanning Electron Microscopy - X-ray Emission (SEM-XRE) have been made on various leaching pachucas and tailings samples. The SEM-XRE results are similar to those given previously (Constable and Snodgrass, 1983) and are not discussed further here. Most of the results discussed here come from the SIMS analyses.

10.1 SIMS Studies

SIMS uses Ar, He or O^- as a primary beam bombarding a small area (40 um - 150 um effective width) which causes ions located on the surface to be sputtered off. This results in a series of energy transfers which emit ions to a gas phase which is subsequently analyzed by mass spectrometry. The ability to continually sputter layer after layer of ions off the same surface area gives a depth profile of the ion density.

In this study, the O^- primary beam was used generally with a beam width of 150 um. The results given in Table 6.1 represent the intensity (in "counts") observed for the different elements. These results cannot be converted directly into relative elemental abundance because the ion yield varies by 2-3 orders of magnitude for different elements. However, using an ion yield curve determined for other geological materials (GSC standard SY-3), an approximate surface concentration can be determined. These values are given for one specimen. For the other samples, the comparison uses the relative differences in number of counts for each element.

There is one substantial problem in interpreting these SIMS results. For normal use, the grain size of a mineral or specimen is of the order of 0.5 mm or larger; with a beam size of 150 um, the beam can be completely contained on one grain. However, the present samples have 20-100 um diameter grains on which are located surface precipitates such as 1 um x 10 um rods. The beam size of 150 um envelopes several grains. Hence, these samples are more properly described as powders. Interpretation of results for powders is problematic because the beam may be just touching the outermost layer of a mill-formed precipitate in one 20 um^2 area while it is viewing a silica solid in another 20 um^2 area of the beam. Hence, depth information must be interpreted qualitatively.

Results are given in Table 10.1 for the following samples:

- (i) side of glass rods exposed alternately to air and to the leaching liquor interface,
- (ii) freshly broken glass rod immersed into the leaching pachuca liquor,
- (iii) silica sand immersed into the leaching pachucas and mounted on coppertape for SIMS analysis,
- (iv) gypsum solids,
- (v) mill solids (leaching pachucas; partial neutralization tank solids, final neutralization tank solids), and
- (vi) tailings (Old Nordic tailings; Lacnor tailings).

The objective of the glass rods and silica sand was to attempt to induce nucleation and crystal growth in the leaching pachucas of silica precipitates on non-ore type, well-characterized surfaces. This allows one to assess the characteristics of nucleation in the leaching pachucas, after comparison with the SIMS analysis on the gypsum solids produced by cooling reactions and on the real leaching pachucas solids. Comparison between fresh tailings and the Nordic Tailings and Lacnor Tailings allows a preliminary evaluation of the effects of weathering and lysimeter experiments on the surface precipitates which remain after weathering.

In this study, the prime concern was to search for Ra-226 and the geochemical mechanism which controls its dissolution behaviour. In this chapter, the prime focus is on barium, lead and sulphur, with calcium, strontium, and iron being of secondary concern. Because all possible elements present are observed by SIMS, within its detection limit, a few comments on their occurrence are also given in this report, particularly for other elements of interest (Al, Si, Th, U).

Data for the glass rods and other experimental solids (Table 10.1a, b, c, d) are reported in terms of the surface analyses or a depth analysis. Data for the other solids (mill solids, tailings) generally are reported for a surface scan, a scan after a 5 minute sputter, and a scan after a 15 minute sputter. These three spectra for the mill solids and tailings are estimated to correspond to the outermost 120 ± 60 nm, a depth of 440 ± 100 nm, and 1,000 ± 200 nm respectively. The depth estimates are based on previous measurements by McIntyre and colleagues at UWO on silicate glass and are only considered accurate within 50%.

TABLE 10.1a INTENSITY (COUNTS) OF ELEMENTS ON DIFFERENT SURFACES ANALYZED WITH SIMS

a) Side of Glass Rod (Inserted in Rio Algom LP)

	Area 1 Splutters	Area 1* (Depth Profile)	Area 2
27 Al	3.5E05	-	1.9×10^5
28 Si	8.8305	4.3E05-1.2E06	9.E05
32 S	8.7E02	8.6E03-9.5E02	5.2E02
40 Ca	1.4E04	-	1.0E04
56 Fe	4.1E06	6.2E04-1.9E04	1.6E04
88 Sr	17	620-87	7.0
138 Ba	180	188-130	96
206 Pb	0.0	-	0.0
232 Th	320	-	6
238 U	170	-	74

TABLE 10.1b INTENSITY (COUNTS) OF ELEMENTS ON DIFFERENT SURFACES ANALYZED WITH SIMS

b) End of Glass Rod (Inserted in Rio Algom Leaching Pachucas)

	Rod 1 Area 1	Rod 1 Area 2 (Depth Profile)	Rod 1 Area 1	Rod 2 Area 2	Rod 1 Area 2	Rod 2 Area 2* (Depth)
27 Al	1.3E05	3.2E05 - 5.2E05	2.0E05	-	1.7E05	5.9E05-5.1E05
28 Si	2.7E05	5.0E05 - 8.8E05	3.6E05	1.7E06-1.4E06	2.7E05	1.2E06-8.7E05
32 S	1.1E03	2.9E04 - 1.0E04	1.4E03	9.5E03-1.9E03	1.9E03	1.3E04-2.6E03
40 Ca	5.5E03	3.1E04 - 2.6E04	8.9E03	-	1.2E04	3.4E04-1.4E04
56 Fe	8.7E03	-	2.3E04	8.1E04-5.5E04	2.1E04	-
88 Sr	9.0	20 - 40	34	80 - 12	17	62-30
138 Ba	36	340 - 230	73	190 - 53	55	190 - 130
206 Pb	0	-	0.0	-	0.0	-
232 Th	4.0	6.6E03 - 1.4E04-8.5E03	67	-	75	308 - 95
238 U	23	1.0E03 - 1.1E04	60	-	63	200 - 68

TABLE 10.1c INTENSITY (COUNTS) OF ELEMENTS ON DIFFERENT SURFACES ANALYZED WITH SIMS

c) Powders Mounted on Copper Tape

	Copper Tape	Powder from Side of Glass Rod on Tape	Gypsum Solid on Tape	Sand Precipitate on Tape *
27 Al	0.00	4.6E05	1.7E05	1.1E06 - 6.2E05
28 Si	1.6E02	5.6E05	5.2E05	2.4E06 - 1.5E06
32 S	9.8E01	4.4E02	2.2E03	2.2E04 - 5.4E03
40 Ca	1.2E02	6.9E03	7.7E03	1.3E05 - 3.3E04
56 Fe	0.00	9.8E03	1.1E05	1.9E05 - 2.3E04
88 Sl	0.00	17	32	1,300 - 510
138 Ba	0.00	150	120	1,400 - 440
206 Pb	0.0	0.0	0.0	-
232 Th	0.0	97	87	13,000 - 9,000
238 U	0.0	180	210	11,000 - 1,400

TABLE 10.1d INTENSITY (COUNTS) OF ELEMENTS ON DIFFERENT SURFACES ANALYZED WITH SIMS

d) Gypsum Solids (on Copper Tape)

	Jan. Sample LP1, Area 1*	Jan. Sample LP1, Area 2*	Jan. Sample LP1, Area 2	Feb. Sample LP5, Area 1	Feb. Sample LP5, Area 2
2.7 Al	-	-	5.9E03	5.7E03	3.3E04
28 Si	6.5E04-4.3E03	2.3E05-2.9E04	7.2E03	1.5E03	5.1E03
32 S	4.0E04-1.7E04	5.7E04-3.0E04	9.0E03	7.2E03	1.1E04
40 Ca	9.4E04-7.8E04	1.4E06-1.4E06	2.9E05	2.0E05	2.8E05
56 Fe	4.2E04-4.1E03	2.4E05-1.7E04	3.2E03	6.4E03	1.1E05
88 Sr	190-120	510-320	120	30	40
138 Ba	31-5	76-28	15	0.00	0.00
206 Pb	80-23	300-93	15	0.00	0.00
232 Th	880-150	4,600-870	30	59	130
238 U	730-220	3,300-760	90	130	250

* Depth Profiles Taken

TALBE 10.1e

INTENSITY (COUNTS) OF ELEMENTS
ON DIFFERENT SURFACES ANALYZED WITH SIMS

e) Mill Solids *

	Leach Tank Surface			Final Neut. Surface			Partial Neut. Surface		
	Surface	After 5 min. Sputter	After 15 min. Sputter	Surface	After 5 min. Sputter	After 15 min. Sputter	Surface	After 5 min. Sputter	After 15 min. Sputter
27 Al	9.0 x E05	3.7E05	4.9E05	1.7E05	1.1E04	5.7E04	1.4E06	6.8E05	3.3E05
28 Si	2.2E06	1.0E06	1.3E06	8.2E05	8.3E05	1.2E06	4.5E06	2.4E05	1.3E06
32 S	3.4E03	1.0E02	7.9E02	3.6E03	1.4E03	7.7E02	1.2E04	2.9E03	1.5E03
40 Ca	1.9E04	7.1E03	5.7E03	2.4E05	9.9E04	7.1E04	9.4E05	3.5E05	2.0E05
56 Fe	4.2E04	2.0E04	1.4E04	1.6E04	1.3E04	7.1E03	4.4E04	2.8E04	1.9E04
88 Sr	55	30	23	42	34	5	130	86	46
138 Ba	528	130	467	75	40	44	911	644	334
206 Pb	7	0	0	0	0	0	0	0	0
232 Th	40	10	22	12	6	4	36	38	67
238 U	85	41	58	16	3	0	43	94	29

TABLE 10.1f

INTENSITY (COUNTS) OF ELEMENTS
ON DIFFERENT SURFACES ANALYZED WITH SIMS

f) Tailings

	Old Nordic Tailings (10-20 cm depth)					Old Nordic Tailings (30-40 cm depth)		
		After 5 min.	After 15 min.	Depth Profile		After 5 min.	After 15 min.	
	Surface	Sputter	Sputter	Surface	37 min.	Surface	Sputter	Sputter
27 Al	3.1E05	6.2E04	1.7E04	5.6E05	5.5E05	4.9E05	4.0E05	1.9E05
28 Si	7.4E06	6.8E06	5.8E06	7.8E05	6.0E05	3.1E06	2.4E06	1.9E06
32 S	6.7E02	1.4E02	8.6E01	5.4E02	6.1E01	8.7E02	3.6E02	3.5E02
40 Ca	1.4E03	1.7E02	8.6E01	4.6E01	8.4E02	7.9E02	3.5E02	3.1E02
56 Fe	2.3E05	1.8E03	5.5E03	1.5E05	8.3E03	9.3E04	2.2E04	3.5E04
88 Sr	19	0	7	-	-	26	23	7
138 Ba	57	15	0	304	230	203	134	63
206 Pb	9	0	0	-	-	58	0	3
232 Th	4	0	0	-	-	0	0	0
238 U	3	0	0	17	0	0	0	7

* Depths estimated as follows: Surface 120 nm; 5 min. 440 nm; 15 min. 1,000 nm.

TABLE 10.1g INTENSITY (COUNTS) OF ELEMENTS ON DIFFERENT SURFACES ANALYZED WITH SIMS

g) Tailings (con'd)

	Lacnor Tailings			
	Surface	After 5 min. Sputter	After 15 min. Sputter	Extended Count
27 Al	1.2E05	2.8E05	2.4E05	-
28 Si	7.0E05	1.1E06	8.9E05	-
32 S	1.9E01	1.4E02	5.0E02	-
40 Ca	5.3E03	1.2E03	3.5E02	-
56 Fe	1.4E06	2.8E05	9.2E04	-
88 Sr	180	50	34	-
138 Ba	580	219	59	-
206 Pb	78	21	0	296
232 Th	0	4	0	81
238 U	18	16	0	32
Comment	-	-	-	NoRa226

Barium

Barium intensities do not show any particular pattern between most of the samples. The end of the glass rod shows an order of magnitude variation between two locations on the same rod. Similarly, the gypsum solids show substantial variation, although the bulk analyses show substantially less variation. Some consistency appears in the mill solids data where a larger gypsum concentration on the final neutralization solid results in an order of magnitude lower concentration of barium compared to the leaching tank and partial neutralization tank solid.

For the old Nordic Tailings (from a 10-20 cm depth in the CCIW lysimeter), the barium intensities are estimated to represent a surface concentration of 100 - 500 ug/g. The depth profile (ion intensity) suggests a surface enrichment in barium, but the estimated concentration range is too wide to allow a sufficiently accurate assessment of the magnitude of surface enrichment particularly because the bulk composition averages 300 ug/g. Hence use of the mass data from the digestion experiment is the only method available for assessing the potential degree of surface enrichment on the leaching pachuca solids.

Lead

Lead is detected in a few samples, but not in many. The ion yields are not sufficiently large with SIMS to be useful for assessing the surface concentrations of lead. There are two exceptions. A large amount is detected on the Lacnor surface, and it is also present in substantial quantities in the gypsum solids.

Calcium, Sulphur

Calcium and sulphur are discussed together because of the presence of substantial amounts of calcium sulphate in all samples. There is one order of magnitude larger amount of calcium and sulphur on the silica sand grains inserted into the leaching pachucas (Table 6.1c) than on the glass rods inserted into the pachucas. The ends of the glass rods have about the same amount as on their sides (Table 6.1a, b). The amount of calcium and sulphur on the silica sand (Table 6.1c) is about the same as on the leaching tank solids, suggesting that they are better model surfaces for studying precipitation phenomena than the glass rods, although the glass rods are more amenable for use in SIMS instrumentation than are the 1 mm sand grains.

Through the mill, the amount of calcium and sulphur on the surface of the solids increases nearly one order of magnitude. The reason that the calcium/sulphur surface concentration is higher on the partial neutralization tank solids than on the final neutralization tank solids is not readily clear, but it may relate to the precipitates in the final tanks having a more porous structure. The increase of silica with depth in the final neutralization tank solids supports this reasoning.

The calcium/sulphur content on the partial and final neutralization tank solids is close to that of the gypsum solids (Table 6.1d). The ion-yield curve suggests that the PN surface concentration of calcium is 1-10%. Comparison of these values with the gypsum solids intensity which are similar, points out the need to recalibrate the ion curve where the calcium content is larger than 10% as in the case of the gypsum solids.

Strontium

The strontium content varies over two orders of magnitude on the side of the glass rod, but is more consistent on the ends. The values are similar for the rest of the solids except for the Old Nordic Tailings (Table 10.1f) which are relatively depleted in Sr compared to the other solids.

Iron

The iron content on the surface of the glass rods is less than that on the surface of the silica sand but similar to that on the surfaces of the gypsum solids and of the mill solids. The substantially higher concentration on the Old Nordic and Lacnor Tailings probably reflects formation of iron hydroxides in situ. The iron content of the surface of the Lacnor sample is almost 100 times greater than on the leach tank surface.

Aluminum and Silica

The higher aluminum content on the silica sand than on the glass rods suggests that the sand is a better nucleation site than the glass rod. But the content is similar on the mill solids and tailings suggesting that the silica sand experiment needs repeating to verify the numbers obtained on the silica sand. However the silica content on the scrappings from the silica sand is similar to that of the other solids while the content on the glass rod is lower. This suggests the need to do more work with both glass rods and silica sand before conclusions can be reached concerning which substrate is better for growth studies.

Of note is the aluminum and silica content in the gypsum solids compared to that on other surfaces. The aluminum content is approximately 10-50 times lower while the silica content is two orders of magnitude lower.

With respect to depth profiles, iron and silica generally follow a similar pattern of decrease with depth on the gypsum solids. Similarly iron and uranium drop in concentration at similar rates on the surface of the Old Nordic tailings.

From the ion yield curve (determined for GSC standard SY-3), the surface content of the Old Nordic Tailings is estimated to be SiO_2 - 90%; Al_2O_3: 2-10%.

Uranium and Thorium

The uranium and thorium contents vary from low (glass rods, mill solids) to undetectable in the Old Nordic Tailings. The surface uranium content of the leach tank and Lacnor tailings is consistent with, or lower than the values of the gypsum solids suggesting that much of the surface content could be associated with gypsum.

The ion-yield curve suggests uranium values of 10-50 ug/g for the surface of the Old Nordic Tailings.

Other Elements Detected

An indepth analysis of peaks on the Old Nordic sample indicates the presence of Li, B, C, Na, Mg, P, K, Sc, Ti, Cr, V, Mn, Cu, Rb, Sr, Y, Zr, Nb, La, Ce, and Nd. Most of these elements decrease with depth as the surface is penetrated (140 nm - 1,000 nm) leaving silica as the only constant intensity.

In contrast, concentrations of many elements on the Lacnor samples (e.g., Na, Mg, Al, K, Ti, V, Cr and Nb) do not decrease with depth and appear to be tied to the silica. But most elements (e.g., Fe, S, the rare earth (REE's), U, Ca, and Zr) decrease by a factor of 10 within 1 um (1,000 nm) of the surface.

Thickness of Surface Layer

The surface precipitates in most of the samples appear to have a thickness of the order of 1 um. That of the leaching tank surface and the final neutrailization surface are also approximately 1 um thick, while those of the partial neutralization tank, the Lacnor surface and the Old Nordic Tailings surface are thicker (1-2 um). These values should be used for comparison purposes and not in an absolute sense because of the nature of these materials (powders).

10.2 Other Studies

The Lacnor and the Old Nordic Tailings were studied by ESCA to look for the presence of jarosite, taking advantage of its ability (i.e., ESCA) to measure Fe^{2+}/Fe^{3+} ratios. There was no evidence for jarosite; the most probable iron minerals present in the Fe^{3+} state are iron hydroxide and hematite (Fe_2O_3). Analysis of a jarosite reference sample also pointed out two anomalies: (i) a substantial amount of lead was present in the reference sample, possibly reflecting the presence of some plumbojarostie, (ii) the S/Fe ratio in the reference sample is approximately 3:2, as opposed to the 2/3 ratio predicted by the unit cell formula for K-jarosite of $KFe_3(SO_4)_2(OH)_6$.

In contrast to the ESCA work and the earlier Mossbauer work, (Constable and Snodgrass, 1983), a courtesy analysis by Swiss colleagues using Mossbauer indicated the presence of jarosite in the Old Nordic Tailings but not in the leaching pachuca solids. Furthermore, reinspection of SEM pictures of scrappings of surface precipitates from the Old Nordic tailings obtained by ultrasonic vibration indicates the presence of 1-2 um cubes whose morphology is consistent with that of jarosite. Thus, it is concluded that we have identifed the presence of jarosite in tailings, but not in leaching pachuca samples. However it does not provide evidence for the importance of jarosite as a controller on Ra-226 behaviour. Nor does it provide evidence for whether the high radium-226 association with jarosite observed by Kaiman (1977) results from Ra-226 dissolution recoprecipitation reactions, or from jarosite growth around a solid particle containing high barium/radium concentrations. It does suggest that jarosite does not form in the leaching pachuca (at least in detectable quantities).

Auger studies were undertaken to attempt to identify overall areas of elevated barium concentrations. No such areas were detected, due to the poor detection limit of Auger. On the leaching pachuca sample, Auger spectroscopy resolved Si, S, O, Ca, K, and Ti. On the Old Nordic sample, Auger resolved Si, Al, K, Fe, O, and traces of S. The traces of S were not highly correlated with Ca.

11.0 EVALUATION OF EQUILIBRIUM THEORY USING EXPERIMENTAL DATA

For Ra-226 to be controlled by a coprecipitation mechanism, the solution must be supersaturated with respect to the parent solid, the parent solid must form, and the parent solid must have an affinity for the metal being coprecipitated. It is our hypothesis that the coprecipitate controlling Ra-226 in tailings milled with the sulphuric acid leach process is formed in the first leaching pachuca tanks.

In the Rio Algom (Nordic Mill) leaching tanks and laboratory digestion experiments, the leaching liquor is supersaturated with respect to calcium sulphate, barium sulphate and lead sulphate. Because Ra-226 is correlated only with Pb and Ba in the experiments (digestion experiment; dissolution experiment on leaching pachuca solids; dissolution experiment on tailings solids), it is concluded that only lead and barium could significantly control Ra-226 behaviour. This does not preclude gypsum formed in the partial neutralization and final neutralization tanks from having Ra-226 associated with it, but rather asserts that gypsum is a minor control on Ra-226 behaviour. Furthermore, the Ra-226 content with gypsum could result from Ra-226 following Ba or Pb coprecipitation within the solids rather than acting on its own because N_{BaSO_4} in the gypsum solids is 3×10^{-5} while N_{PbSO_4} in gypsum solids is 6×10^{-4}.

The thermodynamic theory given in Chapter 4 can be evaluated by examining the solution composition and the Ra-226, Ba and Pb content of the solid phase. One set of data composed of two experiments in this project allows us to make this evaluation -- the observations on leaching liquor concentrations from the February sampling, and the EDTA washing experiments on the solids from this same tank **(the EDTA well-washed leaching pachuca solids).**

From the theory, one predicts that the solid phase composition of radium in the parent crystal (e.g., Ra in $BaSO_4$, denoted as $N_{Ra/Ba}$) is given by

$$N_{Ra/Me} = D \frac{[Ra^{2+}]}{[Me^{2+}]} \qquad (11.1)$$

The leaching tank temperature is 55°C but values for D are estimated by Langmuir and Riese (1985) for 25°C and 100°C. Evaluation of the Distribution Coefficient (D) - temperature relationships according to the van't Hoff model gives values of D at 55°C for $BaSO_4(s)$ of 1.3 and for $PbSO_4(s)$ of 6.1.

From the leaching tank data (Ra^{2+} = 16 Bq/L), one can predict from the theory that the solid state distribution of Ra in $BaSO_4$ is

$$N_{Ra/Ba} = 3.3 \times 10^{-6}$$

and of Ra in $PbSO_4$ is

$$N_{Ra/Pb} = 5.3 \times 10^{-8}$$

Using the EDTA extraction data (EDTA = 10^{-2} M and 10^{-1} M), the observed (actual) value on the solid phase for Ra in $BaSO_4$ is:

$$N_{Ra/Ba} = 0.9 \times 10^{-6}$$

and for Ra in $PbSO_4$ is:

$$N_{Ra/Pb} = 2.6 \times 10^{-7}$$

Hence the ratio of actual to theoretical is

for $BaSO_4$: actual/theory = 0.27

and for $PbSO_4$: actual/theory = 4.9

The calculated theoretical values are quite sensitive to the observed Ra-226 concentrations. In some samples (e.g., Skaeff survey), and an earlier sampling of ours (e.g., December), the Ra-226 activity in the leaching pachucas is higher. In the Skaeff survey, the Ra-226 activity was ca 1,400 pCi/L (51 Bq/L). If a value of 46 Bq/L is used, the resultant theoretical value for $N_{Ra/Ba}$ is 4.6×10^{-6} and for $N_{Ra/Pb}$ is 2.0×10^{-7} resulting in a comparison of actual to theoretical values for $BaSO_4$: actual/theory = 0.20

for $PbSO_4$: actual/theory = 1.3

These results indicate that the Ra content in $BaSO_4$(s) is substantially below the theoretical capacity of barium sulphate (the radium occupies 20 to 30% of the capacity) while the Ra content in $PbSO_4$(s) is marginally to substantially above capacity. For experiments on the same solids and leaching liquor samples, the Ra content is substantially above the $PbSO_4$(s) capacity. Other data in this report could be used to assess this point, but a few further chemical measurements are required to complete the analysis.

Three possible conclusions result from this analysis:

(i) that $PbSO_4$(s) contains most or all of the Ra-226 and is over capacity with the theoretical equilibrium amount;

(ii) that $PbSO_4$(s) contains its equilibrium content of Ra-226 and that the remainder is in the $BaSO_4$(s);

(iii) that $PbSO_4$(s) and $BaSO_4$(s) both contain Ra-226 and are below their equilibrium composition.

Theoretically, it is difficult to see why $PbSO_4$ should exceed its thermodynamic capacity and $BaSO_4$(s) be below its thermodynamic capacity because Ra-226 dissolved in $BaSO_4$ behaves more truly as a solid solution than it does in $PbSO_4$. The most plausible explanation involves the source of the three respective cations from the ore minerals and the kinetics of precipitation.

This explanation can be described as follow. Ra-226 and most of the stable Pb dissolved in the leaching tanks originate from the uranium minerals, being respectively the daughters and stable end products of U-238 decay. Hence the diffusional distance for Ra-226 to undergo coprecipitation with Pb into $PbSO_4$ would be of the order of angstroms. On the other hand, barium is probably contained as a substitute for calcium and other cations in seracite and other feldspars, clays, and micas. Even if these minerals are cemented to uranium minerals, the diffusional distance for Ra-226 towards Ba or vice versa would be in excess of angstroms, and possibly up to a micron in length scale. Accordingly, it is plausible that the coprecipitation kinetics of Ra-226 with Pb would be substantially faster than that of Ra-226 with Ba. Furthermore, because a much smaller percentage of the expected activity of Ra-226 is in solution than that of Ra-228, it is apparent that the transport steps or kinetics involved in Ra-226 coprecipitation must be different than those for Ra-228 coprecipitation. Because lead (Pb-206 from uranium minerals; Pb-208 from thorium minerals) is probably involved in precipitation of both Ra-226 and Ra-228, it is possible that the kinetics of barium dissoltuion and reprecipitation and the codeposition of Ra-226 are faster than the kinetics of dissolution of Ra-228.

Radium behaves more as a perfect solid solution in $BaSO_4(s)$ than in $PbSO_4(s)$. Furthermore the correlation of Ra-226 is stronger with Ba than with Pb in extraction experiments on the leaching pachuca solids. Accordingly, it is most plausible that more Ra is associated with Ba than with Pb. This suggests that either $PbSO_4$ is at capacity and $BaSO_4$ under capacity with respect to Ra-226, or that both are under capacity with respect to Ra-226. Viewed from a kinetic perspective, it is improbable that equilibrium conditions of Ra-226 with Pb in $PbSO_4(s)$ are attained under the obviously rapid dissolution-precipitation conditions involved. Hence, we suggest that the most plausible conclusion is that both $BaSO_4(s)$ and $PbSO_4(s)$ are undercapacity with respect to Ra-226.

The slopes of the regression relationships also provide some insight into the mechanism of coprecipitation. In experiment 4, (the salt dissolution experiment on LP solids) the relationship for the dissolution data of Ba is:

$$\log \text{Ra-226} = 0.910 \log \text{Ba} - 5.92 \qquad (11.2)$$

while the relationship for the dissolution of Pb is

$$\log \text{Ra-226} = 0.989 \log \text{Pb} - 6.54 \qquad (11.3)$$

Hence, at Ba levels of 13.8 mg/L, the observed Ra:Ba ratio is 2.2×10^{-6} while at Ba levels of 0.0138 mg/L, the Ra:Ba ratio is 4.1×10^{-5}. The observed Ra:Pb ratio is 3.1×10^{-7} for Pb levels of 210 mg/L and is 3.2×10^{-7} for Pb levels of 2.1 mg/L. This suggests that the radium content of the first-formed barium sulphate is lower than that of the later-formed barium sulphate, but that the radium content of the first-formed lead sulphate is essentially the same as that of the later-formed lead sulphate. Other regression data shows a wider difference, although some of the values are not significantly different from each other. This variability suggests a kinetic control on the coprecipitation process.

After comparing time scale of dissolution and precipitation in each leaching tank (3 hr) of Rio Algom to the time scales of various precipitation studies in the literature (the lambda, kinetic distribution; and the D, equilibrium distribution), it is our suggestion that the lambda distribution is the most probable distribution for describing Ra-226 distribution in leaching pachucas. Of concern to the modelling objectives of the NUTP is how far the value of lambda deviates from the value of the D distribution coefficient, and how important this deviation is, relative to other uncertainties in modelling geochemical processes in tailings. This point awaits further assessment.

12.0 APPLICATION TO NUTP MODELLING ANALYSIS

This work suggests that a method for modelling dissolution reactions of coprecipitated radium formed in the leaching pachucas is through use of the follow equations for 25°C

$$N_{Ra/Ba} = \lambda_{RaBa} \frac{[Ra^{2+}]}{[Ba^{2+}]} \qquad (12.1)$$

$$N_{Ra/Pb} = \lambda_{RaPb} \frac{[Ra^{2+}]}{[Pb^{2+}]}$$

where $[Ba^{2+}]$, $[Pb^{2+}]$, and $[Ra^{2+}]$ are the concentrations of Ba, Pb and Ra in solution (moles/L).

Provided that equilibrium of the solution with a $BaSO_4(s)$ and $PbSO_4(s)$ are obtained, then the value for $[Pb^{2+}]$ and $[Ba^{2+}]$ can be obtained from the equilibrium reactions

$$Pb^{2+} + SO_4^{2-} = PbSO_4(s) \qquad pK_{so} = 7.7 \qquad (12.3)$$

and

$$Ba^{2+} + SO_4^{2-} = BaSO_4(s) \qquad pK_{so} = 9.97 \qquad (12.4)$$

Activity coefficients and other solution complexes also need to be considered.

With this model, two parameters λ_{RaBa} and λ_{RaPb} and two initial conditions require calibration: N_{RaBa} and N_{RaPb}. The data of this report indicate the following values for

N_{RaBa}: a range of 1×10^{-5} to 1×10^{-7}
N_{RaPb}: a range of 4×10^{-7} to 5×10^{-8}

The actual values of N_{RaBa} are a function of the values of N_{RaPb} because in our experimental data, assignment of a value for N_{RaBa} sets the value for N_{RaPb}. The values of N_{RaBa} and N_{RaPb} will change during tailings dissolution-precipitation reactions if the tailings solid phase composition changes from the values of the experiments. If our experimental data are used, the value of λ_{RaBa} is a function of the value of λ_{RaPb}, again because the value of one defines the value of the other. The actual values of N and λ cannot be defined until a determination can be made of the relative importance of the $BaSO_4(s)$ and $PbSO_4(s)$ as a controller upon Ra-226 and whether equilibrium relationships (as opposed to kinetic relationships) occur in a tailings pile. If equilibrium relationships are eventually reached in the tailings, the values of λ(the kinetically-based distribution coefficient) approach those of D (the equilibrium distribution coefficient). Further analysis of the data of the report after more chemical analysis would aid resolution of these inter dependencies.

13.0 SUMMARY AND RECOMMENDATIONS

13.1 Summary

In this study, the mechanism which controls the dissolution behaviour of Ra-226 in uranium tailings formed by the sulphuric acid leaching process has been assessed using experimental and theoretical approaches. The experimental approaches include laboratory experiments which simulate mill digestion procedures under acid conditions, analyses of the actual leaching data, and dissolution studies on mill solids and tailings using various washing agents (KCl; $CaCl_2$; $BaCl_2$; $FeCl_3$; $HClO_4$; HCl; H_2SO_4; HNO_3; distilled water). The theoretical approaches involve equilibrium calculations for host crystal formation and for the thermodynamics of trace Ra-226 coprecipitation in a parent crystal.

Our hypothesis is that Ra-226 dissolution behaviour is controlled by the dissolution of a parent metal-sulphate crystal with which Ra-226 is coprecipitated. Our initial hypothesis was as follows: of the plausible metal sulphates including those of calcium, iron, barium and lead, barium sulphate was the parent crystal which controlled Ra-226 behaviour. Further analysis of the literature involving studies of calcium interactions with barium sulphate show that strontium might affect radium-226 capture by barium sulphate. Our experimental and theoretical work in this project altered our initial hypothesis to one of Ra-226 dissolution being controlled by $PbSO_4(s)$ and/or $BaSO_4(s)$ with the exact role of one versus the other being unclear.

Experiments on Ra-226

Based on this work, the following points are made concerning solution characteristics in the leaching pachucas and dissolution characteristics of mill solids and U-mill tailings.

1. The leaching pachucas of the Rio Algom Nordic mill are supersaturated with respect to gypsum, lead sulphate, and barium sulphate. In immediately filtered solutions, gypsum precipitates, thereby attaining concentration levels in solution close to those expected at equilibrium, but the solutions remain supersaturated with respect to $BaSO_4(s)$ and $PbSO_4(s)$ for at least one month. This may result

from the formation of submicron sols of these metal sulphates which are measured as "soluble", or from the existance of another phase which alters their "effective solubility product, K_{so}".

2. A sulphuric acid digestion of the ore in the laboratory reasonably simulates observed leaching characteristics in the leaching tanks. A comparison of nitric and perchloric acid digestion of the ore with actual leaching conditions suggests that 3 times more calcium, 10-40 times more barium, and 8-10 times more lead are brought into solution by these leachants than are measured in mill-circuit solution. The extra mass leached in the sulphuric acid leaching solution is assumed to be redeposited on the solids by precipitation as their respective metal-sulphate solids. These calculations provide one basis for estimating the mass of metal sulphates on the surface of tailings, data required for development of a source term model.

3. Of the plausible metal sulphates which could control Ra-226 coprecipitation in solution, Ra-226 activity in the leaching pachucas is correlated only with barium and lead concentrations in the leaching solutions. Furthermore, the solution is supersaturated only with respect to barium sulphate, calcium sulphate and lead sulphate. These are conditions required for Ra-226 behaviour to be controlled by a barium sulphate or lead sulphate solid.

4. In laboratory dissolution experiments on leaching pachuca solids (with EDTA, KCl, $CaCl_2$, $FeCl_3$, HNO_3, $HClO_4$, H_2SO_4), Ra-226 dissolution correlates best with barium dissolution for most experiments, but also quite well with lead. Multiple regression analysis generally results in only barium being significant in the final equation for experiments on any single set of solids.

5. Using EDTA as a dissolving agent, the regression equation relating the dissolved Ra-226 activity to the dissolved barium concentration from leaching pachuca solids, is essentially the same as for solutions using acids (HNO_3, $HClO_4$ H_2SO_4) as the dissolving agents. These regression equations are essentially the same as those for the activity of Ra-226 versus the concentration of barium in the leaching tanks and in the laboratory digestion experiments. This agreement is one method of validating the coprecipitation theory which states that the ratio of Ra/Ba in a coprecipitate is proportional to the ratio in solution.

6. Radium-226 dissolution from tailings samples is better explained by barium dissolution than by lead dissolution for Gunnar and Lacnor tailings (based on the value of r^2).

7. For all data combined, barium better explains Ra-226 dissolution than does lead (based upon the value of r^2). The overall correlation coefficient between Log (Ra) and Log (Ba) is 0.83.

8. Coprecipitation theory, based on thermodynamics and measured leaching pachuas solution conditions, predicts that a barium sulphate coprecipitate and/or a lead sulphate coprecipitate could control Ra-226 dissolution behaviour. In the experiments on the leaching pachucas solids, the ratio of Ra-226 dissolved/Pb dissolved is in excess of the equilibrium capacity of $PbSO_4(s)$ for Ra-226 (150% - 500%) while the ratio of Ra-226 dissolved/Ba dissolved is only 20-30% of the equilibrium capacity of $BaSO_4(s)$ for Ra-226. Other considerations (see Chapter 11) lead to the conclusion that Ra-226 coprecipitation is most probably controlled by kinetics and hence that the amount of Ra-226 in both barite and anglesite is below their respective thermodynamic capacity.

9. An adsorption experiment shows that Ra-226 does not significantly adsorb to leaching pachuca solids (i.e., a tailings analogue) at pH less than one in nitric acid solutions. However it does "sorb" in sulphuric acid solutions with a K_D varying from 160 ml/gm at a solid liquid:ratio of 1:40, to a value of 1 ml/gm at a solid:liquid ratio of 1:1. Because the solutions are supersaturated with respect to these metal sulphates, it is concluded that the "sorption" in sulphuric acid solutions is due to coprecipitation of Ra-226 onto the solid with barium or lead sulphate, rather than due to reversible adsorption.

10. The dependence of K_D on solids concentration has been observed in other aqueous systems, but not satisfactorily explained. Our results suggest a hypothesis that the solids dependency may be explained by the kinetics of coprecipitation in some of these systems. We suggest that one can examine this experimental behaviour with use of a parameter "degree of supersaturation per unit surface area of solid per unit volume of solution".

Coprecipitation theory could be used directly to evaluate the data of this report. But its application to dissolution data is a novel application because the theory is normally applied to precipitate formation, not to precipitate dissolution. Furthermore, the theory is applied to solutions supersaturated with respect to or minimally at equilibrium with the host crystal, whereas the solutions in these dissolution studies were undersaturated with respect to the host crystal ($BaSO_4(s)$; $PbSO_4(s)$). The theory requires further evaluation before it can be applied to the data of this report.

Levels of Other Radionuclides in Leaching Liquor

The mass (activity) of other radionuclides in the leaching pachucas can also be used to assess whether $BaSO_4(s)$ or $PbSO_4(s)$ controls the dissolution behaviour of Ra-226. The ore bodies in the Elliot Lake region are sufficiently old that secular equilibrium should exist between U-238 and its daughters (U-234; Th-230; Ra-226; Pb-210; Po-210) and between Th-232 and its daughters (Ra-228; Th-228). If a portion of an U-238 mineral is dissolved, the same radiological activity of the daughters of U-238 should be found in solution as that of the parent U-238 provided that they are not resorbed or reprecipitated. Similarly, the same radiological activity of the daughters of Th-232 should be found in solution as that of the dissolved Th-232. Hence the amount of U-238 found in solution for U-238 daughters and the amount of Th-232 in solution for Th-232 duaghters are used to define the expected activity of daughters in solution.

Analysis of the leaching tank data and acid digestion experimental data indicate the following:

1. Approximately 0.4% of expected levels of Ra-226, 7.3% of Pb-210 and 3.9% of Po-210 are found in the leaching tanks (Table 3.1 data). Approximately, 0.9% of expected levels of Ra-226, and 4% of Pb-210 and Po-210 (Table 6.1) are found in sulphuric acid leaching experiments in the laboratory. It is the hypothesis of this report that the remainder is dissolved and reprecipitated as a coprecipitate (Ra-226 with $PbSO_4$ and $BaSO_4$; Pb-210 with $PbSO_4$ and possibly $BaSO_4$).

2. In nitric and perchloric acid solutions in the laboratory, only 10-20% of Ra-226, 30-50% of Pb-210 and 5-30% of Po-210 are observed in solution. The solutions are supersaturated with respect to $BaSO_4(s)$ and $PbSO_4(s)$. This suggests that sufficient sulphate is formed to coprecipitate part of these radionuclides which are dissolved as the parent uranium mineral is digested.

3. In the laboratory digestion experiments, 12-25% of expected levels of Ra-228 are observed in sulphuric acid solution while only 0.7 to 1% of expected levels of Ra-226 are observed. This suggests that the kinetics of Ra-226 coprecipitation are different than the kinetics of Ra-228 coprecipitation. Because stable Pb is located physically quite close to Ra-226 (being the final decay daughter of the U-238 chain), it would appear to be physically easier for Pb to capture Ra-226 than for Ba to capture Ra-226 in a metal sulphate because barium is probably located physically further from Ra-226. Some mineralogical analysis etc., is required to identify the distance of Ba from Ra-226.

4. In the laboratory-experiments and leaching-pachuca data, 4-8% of Pb-210 and 4% of Po-210 remains in sulphuric acid solution whereas Ra-226 levels are 0.1-1%. Because Pb-210 and stable Pb-206 should act in a chemically similar fashion and because they are located close to each other in the uranium mineral, it is expected that a similar ratio of Pb-210 and stable Pb dissolved from the uranium mineral should be reprecipitated. A comparison of Pb-210 and stable Pb concentration in the nitric acid/perchloric acid solutions with those in sulphuric acid solutions shows that similar amounts are reprecipitated in sulphuric acid solutions. But the amount of Pb-210 reprecipitated is much smaller than for Ra-226. This suggests that formation of another coprecitate such as barium sulphate is required to explain the extra amount of Ra-226 removed from solution, compared to the amount of Ra-228 coprecipitated. This assumes that the kinetics of $PbSO_4$ precipitation are such that similar activities of Pb-210 and Ra-226 are coprecipitated with $PbSO_4$.

Hence, in summary, observations on other radionuclide levels in acid leaching solutions indicate that the activity of Ra-228 observed in solution compared to its expected activity is substantially larger than the activity of Ra-226 observed in solution compared to its expected activity. Both Ra-226 and Ra-228 should act similarly in solution from a chemical perspective. The different ratios of observed/expected must result from different rates of coprecipitation. The most plausible explanation is that Ra-226, Pb-206 and Ba dissolve and reprecipitate before substantial amounts of Ra-228 and Pb-208 dissolve and reprecipitate. A complete explanation must account for the point that the diffusional distance of Ra-226, Pb-210 and Pb for precipitation in $PbSO_4(s)$, may be of order of angstroms, because these three are at the same lattice sites in the uranium mineral, while the diffusional distance for Ra-226 diffusion to a barium ion may be larger. However, it is probable that coprecipitation kinetics are influenced mostly by solution concentrations, rather than local concentrations within fluid films around the leaching minerals.

General Summary

It is concluded that barium sulphate better explains Ra-226 solid-solution behaviour than does lead sulphate. But this cannot be stated as an unambiguous conclusion. The mineralogical origins of Pb and Ba and the fate of other radionuclides during the leaching process will provide additional evidence for determining the relative importance of each. Further dissolution experiments involving other chemical agents which appear to have chemical selectivity for barium are required to completely define the relative importance.

13.2 Recommendations for Further Work

The following represent a suggested scope of work for defining which metal precipitate controls Ra-226 dissolution behaviour.

1. Additional measurements on solids and experimental solutions used in this study. These measurements were not made previously because of time and budget constraints but would provide additional insights into the mechanism controlling Ra-226 dissolution. These suggested measurements are detailed elsewhere.

2. Use monitoring data from the groundwater and surface water runoff to check the theory and its calibration outlined in this report. Develop the data of this report, the further chemical measurements, and the monitoring data into parameter values and their distributions for the modelling efforts of probabilistic assessment.

3. Evaluate why the solutions (leaching pachuca liquor) appear to remain supersaturated with respect to barium sulphate and lead sulphate for at least a month. This could involve incorporation of Pitzer's modification for calculation of ion activity coefficients and/or developing experiments to ascertain a rationale for this phenomena. A useful experiment would be to more correctly measure the pH of these solutions (pH LT 0.5). The possible longterm maintainance of supersaturation conditions could negate an assumption of equilibrium conditions for source term model development.

4. Use other extraction agents with a higher degree of chemical selectivity to attempt to dissolve only $PbSO_4$ or $BaSO_4$.

5. Continue experiments not completed on this study involving distilled water to attempt to selectively dissolve $PbSO_4$ compared to $BaSO_4$. Their different solubility products give a large degree of chemical selectivity to dissolution. The major variable is the experimental time, since large quantities of distilled water are required.

6. Carry out desorption experiments after an adsorption experiment to confirm that "sorption" in sulphuric acid is not reversible adsorption, but rather coprecipitation.

7. Design measurements to evaluate the aspects given below. The understanding developed by these measurements should give a scientific base for modelling Ra-226 dissolution in tailings. The measurements are:

   (i) Identify the minerals from which radium, lead, barium, and other elements of concern are derived, using standard mineralogical and micro-mineralogical techniques.

   (ii) Identify the solids formed, the species in solution, their mineralogical sources, and the concentrations of each over time as the ore dissolves.

   (iii) Identify the fate of each of these solids and species in the process stream.

(iv) Identify the surface precipitate (host crystal) containing Ra-226 and Ra-228 with direct observational techniques and identify the crystallization site.

(v) Evaluate and quantify the kinetics of dissolution of mono-minerals containing Ra-226, Ra-228, Ba, Pb, Ca, Fe and Sr.

(vi) Numerically simulate these coprecipitation kinetics using data from simple laboratory systems to evaluate Ra-226/Ra-228 differences.

(vii) Evaluate steps (v) and (vi) in the heterogeneous mill system.

(viii) Couple steps (v), (vi) and (vii) with an evaluation of supersaturation conditions in the mill of the relevant parent crystal.

(ix) Validate that the same host solid controlling Ra-226 in the leaching pachua solids also controls its dissolution behaviour in old tailings.

(x) Trace the fate of each of the solids and soluble species in the mill processing streams from the time of placement of the tailings behind their containment structure, to the present.

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APPENDIX 1

Calcium, Barium, and Radium (Co), Deposition Durng the Winning of Uranium Ores — A Literature Review of Fundamental Studies onthe Contamination of Precipitates from Solution

CALCIUM, BARIUM AND RADIUM (CO) DEPOSITION DURING THE WINNING OF URANIUM FROM CANDIAN ORES -- A LITERATURE SURVEY OF FUNDAMENTAL STUDIES ON THE CONTAMINATION OF PRECIPITATES FROM SOLUTION

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Abstract

The various models of coprecipitation are reviewed and are illustrated with examples taken from radium/barium/calcium systems. A summary of the data collected from coprecipitation studies on these same systems with several anions is presented. A method for the activation of barium sulfate toward sorption of radium and strontium is reported.

1.0 INTRODUCTION

The leaching of Radium-226 from mine tailings is a serious environmental problem associated with the winning of uranium from Canadian ores. From process plant data gathered over the past ten years at the Rio Algom mill, one can suggest that, in the first leaching pachuca, the radium is mobilized from its feed mineral(s) and is then precipitated out on the surface of insoluble quartz particles. The particles continue through the process plant gathering additional surface coatings made up primarily of calcium sulfate. These are separated from the process liquor and are eventually rejected as tailings. Data from surface analyses of sample particles taken from several points in the process plant are not inconsistent with this model. The details of the mechanism of the (co)deposition of radium-226 in the first leaching pachuca, however, are not known. Thus, a method of intervention that would either permanently immobilize the radium-226 on the quartz surface or prevent its deposition thereon cannot be specified.

To design experiments that will produce data useful for modeling the deposition of radium in the first pachuca, background information on the various general models of contamination of precipitates from solution as well as data taken from studies on the calcium/barium, calcium/radium and barium/radium coprecipitation systems must be in hand. The results of a literature survey designed to search out this background information will be presented in this report.

2.0 MODELS OF THE CONTAMINATION OF PRECIPITATES FROM SOLUTION

Under the general rubric "contamination of precipitates from solution" one finds both the intentional and the unintentional bringing down with a host crystal some foreign species present in the mother liquor. The general terms used in the description of data observed during studies in this area are:

-coprecipitation--the foreign species is not supersaturated with respect to the mother liquor but it is brought down with the host crystal by one or more of adsorption, occlusion (entrapment) and inclusion (mixed crystal formation or solid solution formation);

-post precipitation--the foreign species is supersaturated with respect to the mother liquor but it forms crystals much later in time than the host crystals; and,

-gathering--the foreign species is supersaturated with respect to the mother liquor and forms crystals simultaneously with the host.

From the limited data available on the solubility of the various species present in the process plant liquor, I would suggest that the deposition of radium from solution is via one or more of the coprecipitation processes noted above. For modeling studies, these may be grouped into four categories; namely,equilibrium or non-equilibrium reactions with miscible or immiscible solid state components. These will be examined below.

2.1 Miscible Components in the Solid State (Inclusion):

If a precipitate forms in the presence of a foreign ion with which it forms an ideal solid solution, this foreign ion will be incorporated into the growing crystal even though the solubility of the pure phase formed by that foreign ion is not exceeded in the solution under consideration. Thermodynamically, the free energy of mixing describes the potential for coprecipitation in such ideal systems. This is illustrated by Figure 1. Most solid solutions exhibit an heat of mixing and a volume change on mixing and deviate from the ideal case to greater or lesser extents. This is illustrated in Figure 2. The coprecipitation of radium with calcium sulfate, calcium with barium sulfate and barium with calcium sulfate follow the limited solid solution curve and that of radium with barium follows the complete solid solution curve.

2.1.1 Reactions at Equilibrium:

When a solid and solution are at equilibrium, each component capable of transport from one phase to the other must have the same chemical potential in the two phases. The efficiency of coprecipitation, however, depends upon a number of experimental factors which include the extent of similarity of the ions involved and the method and rate of precipitation. Even so, the distribution of the impurity in the carrier substance can usually be described by a "limiting law"; namely, the Berthelot-Nernst (homogeneous) distribution law. In this model it is assumed that the whole crystal is in equilibrium with the final solution. From this it follows that the impurity is homogeneously distributed through out the crystal. Equation 1 and Figure 3, represent this model.

------a. $A_{xtal} + B_{soln} \rightleftharpoons A_{soln} + B_{xtal}$

1.

------b. $D = \dfrac{A_{soln} \times B_{xtal}}{A_{xtal} \times B_{soln}}$

2.1.2 Reactions not at Equilibrium:

At least three "kinetic" processes are involved in cyrstallization: mass transport through the solution to the surface of the growing crystal, reaction(s) at the surface, and diffusion through the solid. The latter is usually a very slow process; thus, the surface of the crystal only will be in equilibrium with the solution to which it is exposed. This gives rise to a layered distribution within the crystal with each layer having is own impurity level--much like an onion. This can also be described by a limiting law--the Doerner-Hoskins (logarithmic) distribution law. It is represented by Equation 2 and Figure 3.

------a. $A_{xtal} + B_{soln} \rightleftharpoons A_{soln} + B_{xtal}$

2.

------b. $\lambda = \log\left[\frac{A_{initial} \times B_{final}}{A_{final} \times B_{initial}}\right]$ initial/final = soln concs.

2.1.3 General Comments:

At present, there is no method for predicting if D and λ will be greater than one (an enrichment system), equal to one (no change from the solution composition), or less than one (a derichment system). One can direct the system toward a given distribution of the impurity in the host crystal by the method used to carry out the precipitation. Very rapid mixing of reagent solutions at room temperature followed by long standing or very slow precipitation from undisturbed supersaturated solution leads usually to experimental data with which the homogeneous distribution law is consistent. Slow isothermal evaporation or the slow generation of the precipitating reagent _in situ_ usually gives rise to data with which the logarithmic distribution law is consistent. This is illustrated in Figure 4.

2.2 Immiscible Components in the Solid State (Adsorption and Occlusion):

Adsorption is probably one step in all crystal growth processes. Growing crystals tend to adsorb preferentially species of their own kind or foreign species that fit naturally into the host crystal lattice. Under the conditions of high surface area and/or high solution concentration of foreign species that do not fit into the host lattice and/or high surface charge and/or rapid rate of precipitation, the tendency to be selective may be overcome. The adsorbed foreign species become trapped in the host crystal and are brought down with the precipitate. Such processes, under very closely controlled solution conditions, have been shown to follow one or more of the empirical adsorption isotherms shown as Figure 5. As with most interfacial phenomenon, subtle changes in experimental conditions may give rise to dramatic changes in the observed data. Aging (Ostwald ripening) leads to expulsion of the trapped foreign species and to a decrease in the surface area of the precipitate.

3.0 RESULTS OF LABORATORY STUDIES

The results of classical coprecipitation studies with radium as the trace component are summarized in Figures 6-11 and in Table 1. Both "D" and "λ" behaviors are observed. Lambda behavior seems to predominate, however, and should be anticipated in the process liquor if a mixed crystal model is being followed.

In a series of papers by Berak, et al, it is reported that barium sulfate can be "activated" for the sorption of strontium and radium by heat treatment with calcium sulfate. The rate of radium/strontium capture may be approximated by the laws of diffusion into a sphere with a constant of 2.6x10(exp-9) cm(exp2)/sec. The solid is selective toward Ra and Sr against Ca. This suggests that the extraction of calcium from barium containing minerals will "activate" them toward radium and strontium sorption in the process liquor. Also, it suggests that extraction of barium from calcium minerals may activate them toward sorption of radium and strontium, as well.

Table 1. Homogeneous Coprecipitation of Radium with Various Sulfates.

Host	Trace	Di(λ)*	Temp.
$CaSO_4$	^{224}Ra	< 0.01	Hot
$CaSO_4 \cdot 5H_2O$	"	∿ 0.	-
$BaSO_4$	"	1.8	20°C
K_2SO_4	"	15-30	-
Rb_2SO_4	"	15-30	-
Ag_2SO_4	"	∿ 0	Room
$MgSO_4 \cdot 7H_2O$	"	∿ 0	-
$BaSO_4$	"	(1.21)	90°C
$BaCrO_4$	"	(5.50)	0°C

* Defined elsewhere in this report.

Figure 1. Partial and Total Free Energies of Mixing in Ideal Solutions (Ba and Ra Sulfates).

Figure 2. Partial Molar Free Energy of a Solute in Two Typical Solid Solutions (Ca and Ra Sulfates follow the Limited Solid Solution).

Figure 3. Distribution Curves for D and λ.

Figure 4. The Influence of Rate of Precipitation.

a) Schematic diagram for the effect of precipitation rate on the distribution coefficient λ. In enrichment systems $\lambda \rightarrow \lambda_1 = D_1$, as the precipitation rate → 0; for fast rates of precipitation $\lambda \rightarrow \lambda_3 = 1$. For depletion systems an analogous situation exists with $\lambda \rightarrow \lambda_1 = D$ for close to zero precipitation rates and $\lambda \rightarrow \lambda_3 = 1$ for rapid precipitation.

b) The effect of precipitation velocity on the value of the distribution coefficient λ.

Figure 5. Adsorption Isotherms. (S = "S" shaped; L = Langmuir; H = high affinity; and, C = Constant partition.)

Figure 6. Slow evaporation from saturated solutions. System: barium-radium chlorides. Temperature: 20± 0.2°C.

Figure 9. Precipitation of barium-radium carbonates from homogeneous solution.

Figure 10. Crystallization of barium-radium nitrates from supersaturated solutions. Temperature: 20 ± 0.2°C.

Figure 11. Coprecipitation of several barium-radium salts.

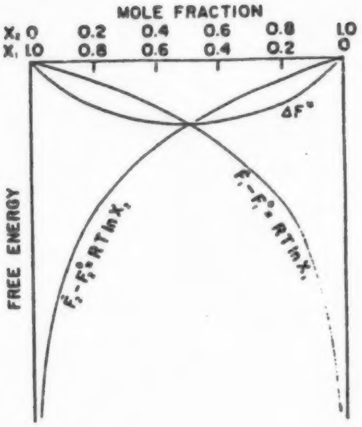


Figure 1

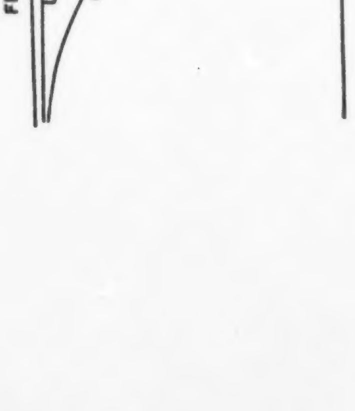


Figure 2

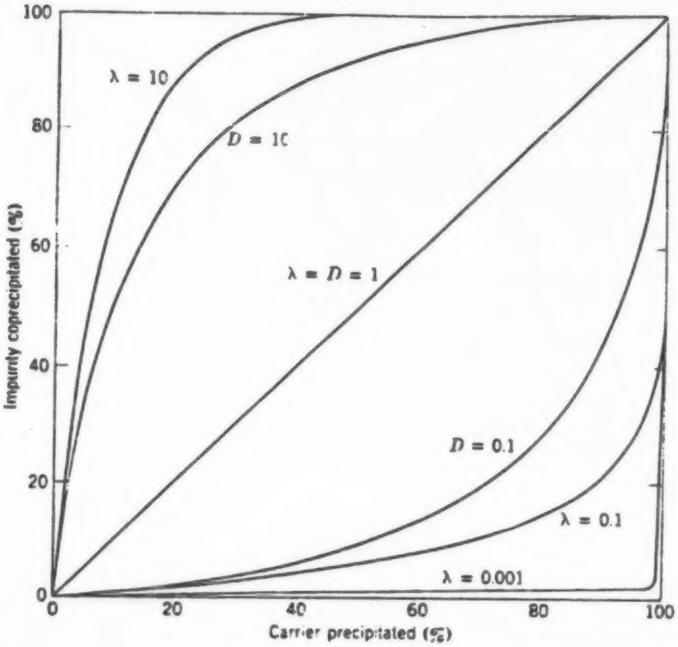


Figure 3

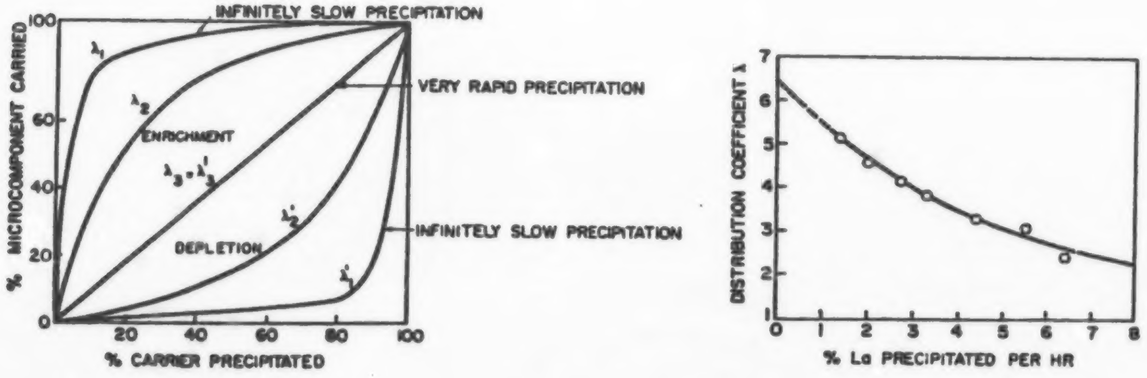


Figure 4 (a)

(b)

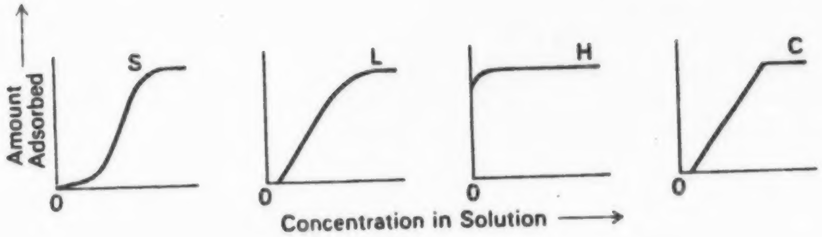


Figure 5

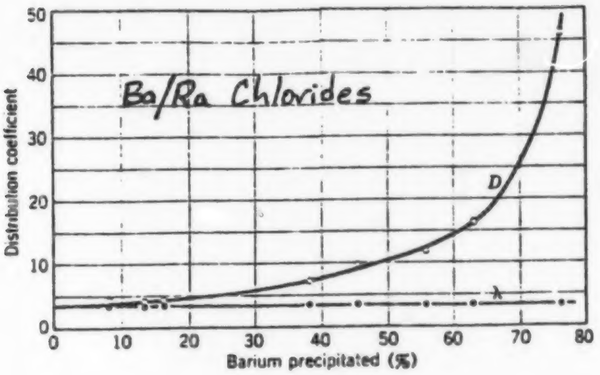


Figure 6

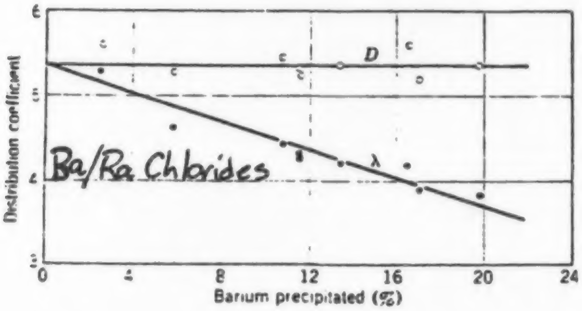


Figure 7

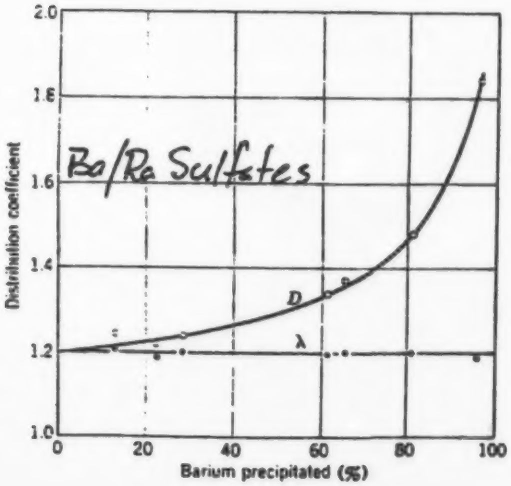


Figure 8

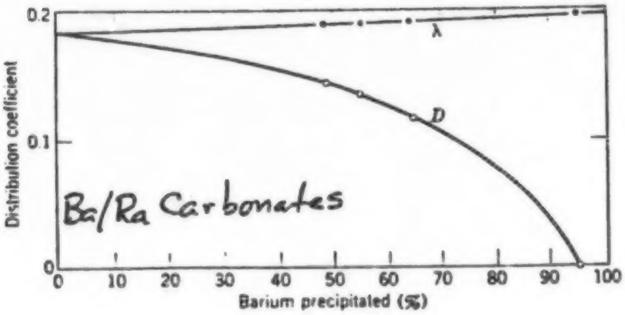


Figure 9

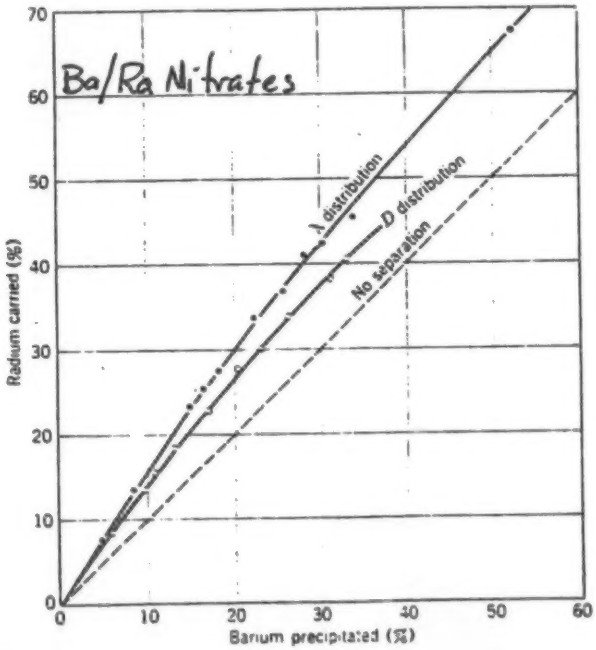
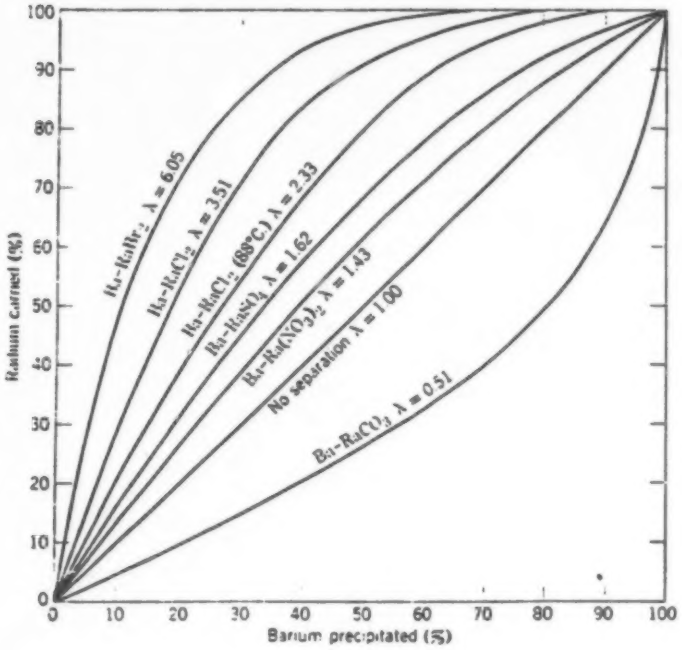


Figure 10



Radium carried (%)
Barium precipitated (%)
0
10
20
30
40
50
60
70
80
90
100
Ba-RaBr$_2$ λ = 6.05
Ba-RaCl$_2$ λ = 3.51
Ba-RaCl$_2$ (88°C) λ = 2.33
Ba-RaSO$_4$ λ = 1.62
Ba-Ra(NO$_3$)$_2$ λ = 1.43
No separation λ = 1.00
Ba-RaCO$_3$ λ = 0.51

Figure 11

APPENDIX 2

Additional Regression Analyses

A.1(a) Plot of Ra with Ca from Digestion Experiment

```
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
          I                                                                11    I
          I                                                              1       I
   -10.125+                                                                      +
          I                                                              1       I
          I                                                                1 1   I
          I                                                                 2    I
          I                                                                      I
     -10.5+                                                                      R
          I                                                                      I
          I                                                              1       I
 L        I                                                                      I
 o        I                                                               1      I
 g -10.875+                                                                      +
          I       1                                                              I
 o        I               1                                                      I
 f        I                                                                      I
          I   1     11                                                           I
 R  -11.25+                                                                      +
 a        I                                                                      I
 d        I                                                                      I
 i        I                1                                                     I
 u        R                                                                      I
 m -11.625+                                                                      +
 -        I                                                                      I
 2        I                                                                      I
 2        I                                                                      I
 6        I                                                                      I
       -12+                                                                      +
 M        I  1                                                                   I
          I                                                                      I
          I                                                                      I
          I                                                                      I
   -12.375+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                  1                   I
          I                                                                      I
    -12.75+                                                                      +
          I                                                                      I
          I                                                  1                   I
          I                                                                      I
          +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
            -2.875      -2.625   -2.375     -2.125   -1.875     -1.625   -1.375
            -3     -2.75      -2.5     -2.25        -2     -1.75      -1.5

                                      Log of Calcium M

19 cases plotted. Regression statistics of RA on CA:
Correlation  .48586 R Squared  .23606  S.E. of Est     .76977 Sig.  .0349
Intercept(S.E.)   -9.66116(   .57588)  Slope(S.E.)     .63059(   .27513)
```

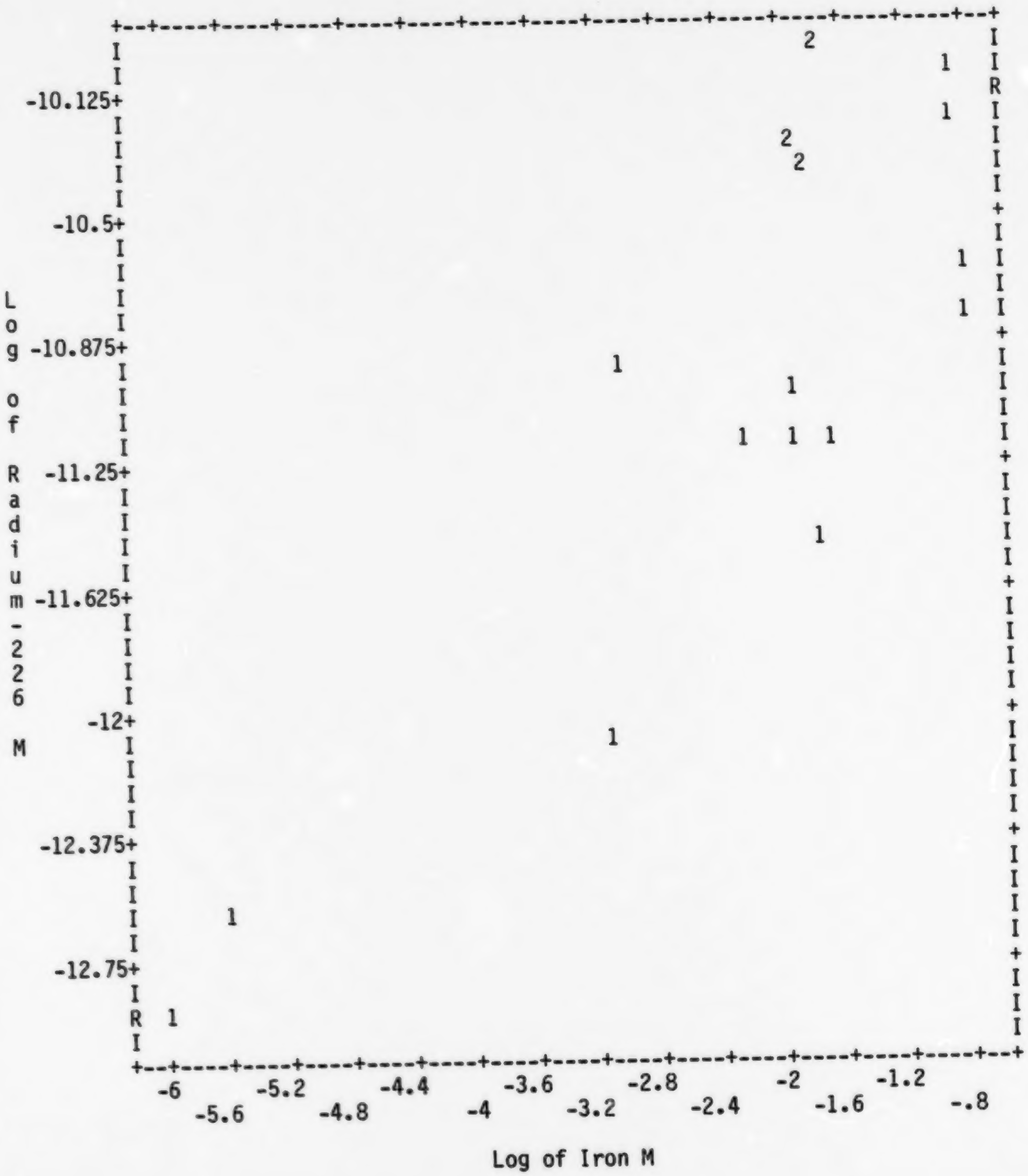
A.1(b) Plot of Ra with Sr from Digestion Experiment

```
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
          I                                                               1 1    I
          I                                                                  1   I
   -10.125+                                                                      +
          I                                                                  1   I
          I                                                        1   1         I
          I                                                             2        R
          I                                                                      I
     -10.5+                                                                      +
          I                                                                      I
          I                                                              1       I
 L        I                                                                      I
 o        I                                                               1      I
 g -10.875+                                                                      +
          I          1                                                           I
 o        I                                   1                                  I
 f        I                                                                      I
          I          1                        2                                  I
 R  -11.25+                                                                      +
 a        I                                                                      I
 d        I                                                                      I
 i        I                                        1                             I
 u        I                                                                      I
 m -11.625+                                                                      +
 -        I                                                                      I
 2        I                                                                      I
 2        I                                                                      I
 6        I                                                                      I
       -12R                                                                      +
 M        I    1                                                                 I
          I                                                                      I
          I                                                                      I
          I                                                                      I
   -12.375+                                                                      +
          I                                                                      I
          I                                      1                               I
          I                                                                      I
          I                                                                      I
    -12.75+                                                                      +
          I                                                                      I
          I                                                  1                   I
          I                                                                      I
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
               -6.125    -5.875    -5.625    -5.375    -5.125    -4.875    -4.625
           -6.25        -6     -5.75      -5.5     -5.25        -5     -4.75

                                     Log of Strontium M

19 cases plotted. Regression statistics of RA on SR:
Correlation  .56123 R Squared  .31498  S.E. of Est       .72893 Sig.  .0124
Intercept(S.E.)   -6.02247(  1.75878)  Slope(S.E.)       .94313(   .33733)
```

A.1(c) Plot of Ra with Fe from Digestion Experiment



```
19 cases plotted. Regression statistics of RA on FE:
Correlation  .82300 R Squared  .67733  S.E. of Est     .50028 Sig.  .0000
Intercept(S.E.)   -9.82677(   .21566) Slope(S.E.)      .49637(   .08309)
```

A.1(d) Plot of Pb with Ca from Digestion Experiment

```
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
         I                                                              2       I
         I                                                              11      I
         I                                                                1     I
   -3.375+                                                                 1    +
         I                                                                 2    I
         I                                                                1 1   R
         I                                                                      I
         I                                                                      I
    -3.75+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
L  -4.125+                                                                      +
o        I                                                                      I
g        I                                                                      I
         I                                                                      I
o        I                1                                                     I
f    -4.5+           1                                                          +
         I    1     1    1                                                      I
L        I       1                                                              I
e        I                                                                      I
a        I                                                                      I
d  -4.875+                                                                      +
         R   1                                                                  I
M        I                                                                      I
         I                                                                      I
         I                                                                      I
    -5.25+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
   -5.625+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
       -6+                                                  1                   +
         I                                                  1                   I
         I                                                                      I
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
            -2.875    -2.625    -2.375    -2.125    -1.875    -1.625    -1.375
           -3     -2.75      -2.5     -2.25        -2     -1.75      -1.5

                                    Log of Calcium M

19 cases plotted. Regression statistics of PB on CA:
Correlation  .57240 R Squared  .32764  S.E. of Est    .77413 Sig.  .0104
Intercept(S.E.)  -2.50611(  .57914) Slope(S.E.)     .79636(  .27669)
```

A.1(e) Plot of Pb with Ba from Digestion Experiment

```
        +----+----+----+----+----+----+----+----+----+----+----+----+--R-+----++
        I                                                               2      I
        I                                         1  1                         I
        I                                                                 1    I
  -3.375+                                                                 1    +
        I                                            2                         I
        I                                            1 1                       I
        I                                                                      I
        I                                                                      I
   -3.75+                                                                      +
        I                                                                      I
        I                                                                      I
        I                                                                      I
        I                                                                      I
L -4.125+                                                                      +
o       I                                                                      I
g       I                                                                      I
        I                                                                      I
o       I                           1                                          I
f   -4.5+                           1                                          +
        I    1           1                    1                                I
L       I                                           1                          I
e       I                                                                      I
a       I                                                                      I
d -4.875+                                                                      +
        I       1                                                              I
M       I                                                                      I
        I                                                                      I
        I                                                                      I
   -5.25+                                                                      +
        I                                                                      I
        I                                                                      I
        R                                                                      I
        I                                                                      I
  -5.625+                                                                      +
        I                                                                      I
        I                                                                      I
        I                                                                      I
        I                                                                      I
      -6+    1                                                                 +
        I       1                                                              I
        I                                                                      I
        +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
            -6.475    -6.125    -5.775    -5.425    -5.075    -4.725    -4.375
         -6.65      -6.3     -5.95      -5.6     -5.25      -4.9     -4.55

                                   Log of Barium M
```

```
19 cases plotted. Regression statistics of PB on BA:
Correlation  .85038 R Squared  .72315  S.E. of Est     .49675 Sig.  .0000
Intercept(S.E.)    1.74778(   .88384) Slope(S.E.)    1.05911(   .15894)
```

A.1(f)

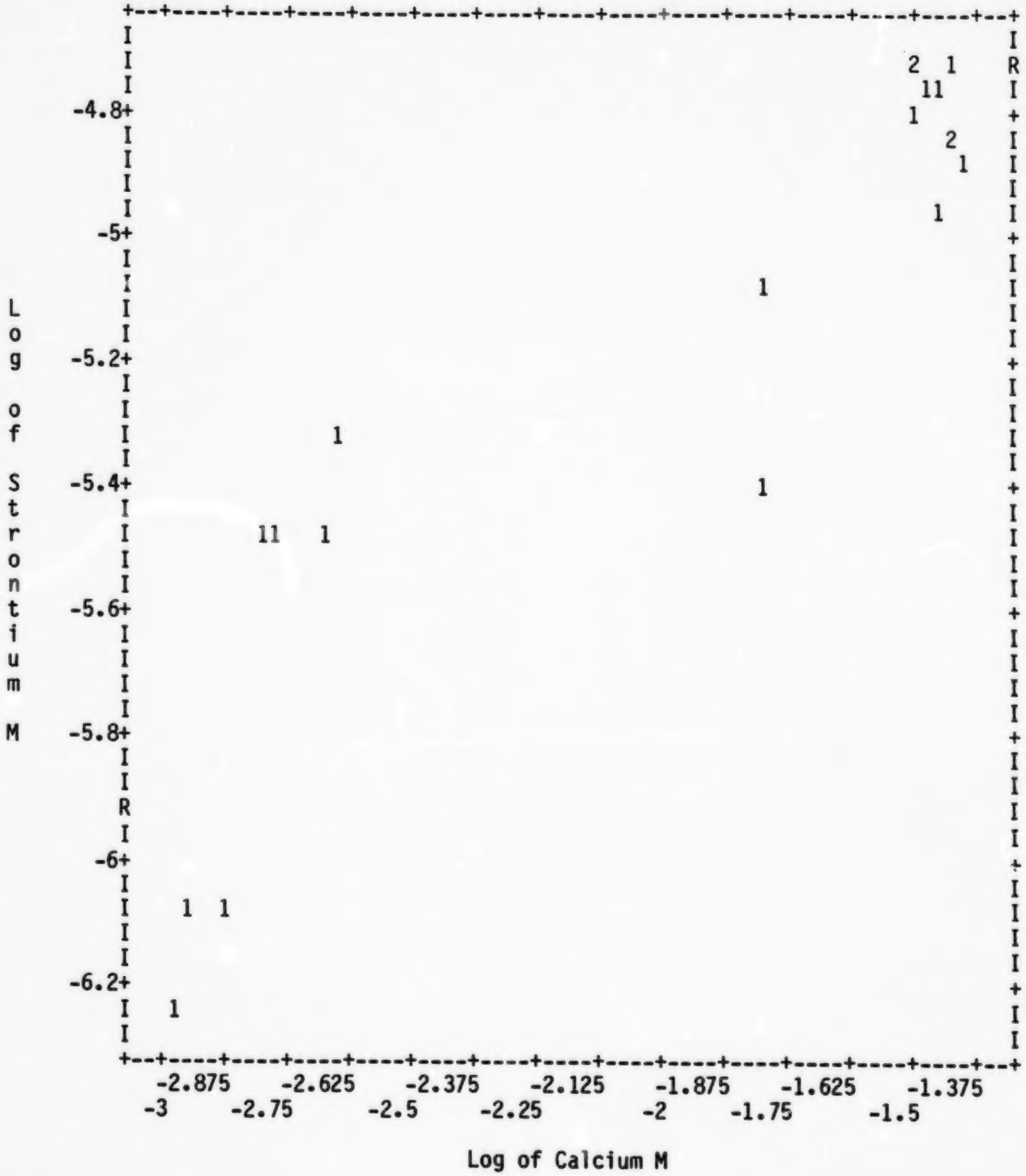
Plot of Pb with Sr from Digestion Experiment

```
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
          I                                                                  2   I
          I                                                              11      I
          I                                                               1      I
    -3.375+                                                                 1    +
          I                                                             2        R
          I                                                        1   1         I
          I                                                                      I
          I                                                                      I
     -3.75+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
 L  -4.125+                                                                      +
 o        I                                                                      I
 g        I                                                                      I
          I                                                                      I
 o        I                                        1                             I
 f    -4.5+                                   1                                  +
          I          1                        2                                  I
 L        I          1                                                           I
 e        I                                                                      I
 a        I                                                                      I
 d  -4.875+                                                                      +
          I    1                                                                 I
 M        I                                                                      I
          I                                                                      I
          I                                                                      I
     -5.25+                                                                      +
          I                                                                      I
          I                                                                      I
          R                                                                      I
          I                                                                      I
    -5.625+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
        -6+                                      1                               +
          I                                                  1                   I
          I                                                                      I
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
               -6.125    -5.875    -5.625    -5.375    -5.125    -4.875    -4.625
           -6.25        -6     -5.75      -5.5     -5.25        -5     -4.75

                                     Log of Strontium M

19 cases plotted. Regression statistics of PB on SR:
Correlation  .65180 R Squared  .42484  S.E. of Est     .71599 Sig.  .0025
Intercept(S.E.)    2.00142( 1.72756) Slope(S.E.)    1.17416(  .33135)
```

A.1(g) Plot of Sr with Ca from Digestion Experiment



```
19 cases plotted. Regression statistics of SR on CA:
Correlation  .91532 R Squared  .83780  S.E. of Est     .21107 Sig.  .0000
Intercept(S.E.)   -3.78178(   .15790)  Slope(S.E.)     .70692(   .07544)
```

A.1(h) Plot of Sr with Ba from Digestion Experiment

```
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
          I                                                                      I
          I                                                               2 1    R
          I                                         1                       1    I
      -4.8+                                            1                         +
          I                                            2                         I
          I                                              1                       I
          I                                                                      I
          I                                            1                         I
        -5+                                                                      +
          I                                                                      I
          I       1                                                              I
L         I                                                                      I
o         I                                                                      I
g     -5.2+                                                                      +
          I                                                                      I
o         I                                                                      I
f         I                           1                                          I
          I                                                                      I
S     -5.4+    1                                                                 +
t         I                                                                      I
r         I    1           1          1                                          I
o         I                                                                      I
n         I                                                                      I
t     -5.6+                                                                      +
i         I                                                                      I
u         I                                                                      I
m         R                                                                      I
          I                                                                      I
M     -5.8+                                                                      +
          I                                                                      I
          I                                                                      I
          I                                                                      I
          I                                                                      I
        -6+                                                                      +
          I                                                                      I
          I                                     1     1                          I
          I                                                                      I
          I                                                                      I
      -6.2+                                                                      +
          I       1                                                              I
          I                                                                      I
          +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
              -6.475    -6.125    -5.775    -5.425    -5.075    -4.725    -4.375
          -6.65      -6.3     -5.95      -5.6     -5.25      -4.9     -4.55

                                     Log of Barium M

19 cases plotted. Regression statistics of SR on BA:
Correlation  .59137 R Squared  .34971  S.E. of Est      .42262 Sig.  .0077
Intercept(S.E.)  -2.93553(  .75195) Slope(S.E.)      .40886(   .13522)
```

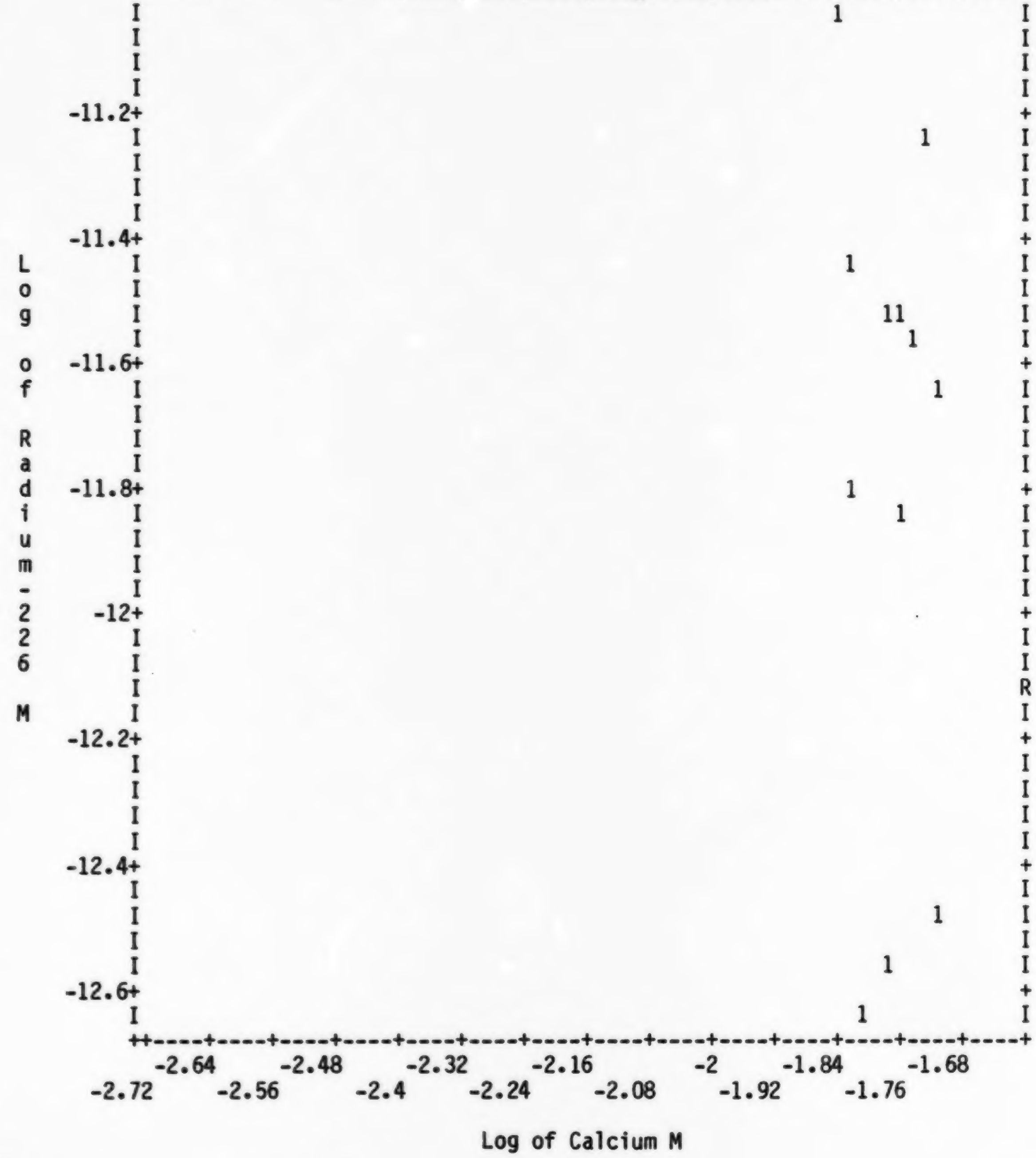
A.1(i) Plot of Ca with Ba from Digestion Experiment

```
         +----+----+----+----+----+----+----+----+----+----+----+----+----+---R++
     -1.4+                                              1                       +
         I                                            3                    2    I
         I                                         1  1                  2      I
         I                                                                      I
         I                                                                      I
     -1.6+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
     -1.8+    1  1                                                              +
         I                                                                      I
L        I                                                                      I
o        I                                                                      I
g        I                                                                      I
       -2+                                                                      +
o        I                                                                      I
f        I                                                                      I
         I                                                                      I
C        I                                                                      I
a    -2.2+                                                                      +
l        I                                                                      I
c        I                                                                      I
i        I                                                                      I
u        I                                                                      I
m    -2.4+                                                                      +
         I                                                                      I
M        I                                                                      I
         I                                                                      I
         I                                                                      I
     -2.6+                                                                      +
         I                           1                                          I
         R                1                                                     I
         I                                                                      I
         I                                                                      I
     -2.8+    1                      1                                          +
         I                                                                      I
         I                                           1                          I
         I                                                                      I
         I       1                             1                                I
       -3+                                                                      +
         +----+----+----+----+----+----+----+----+----+----+----+----+----+----++
              -6.475    -6.125    -5.775    -5.425    -5.075    -4.725    -4.375
          -6.65      -6.3     -5.95      -5.6     -5.25      -4.9     -4.55

                                     Log of Barium M
```

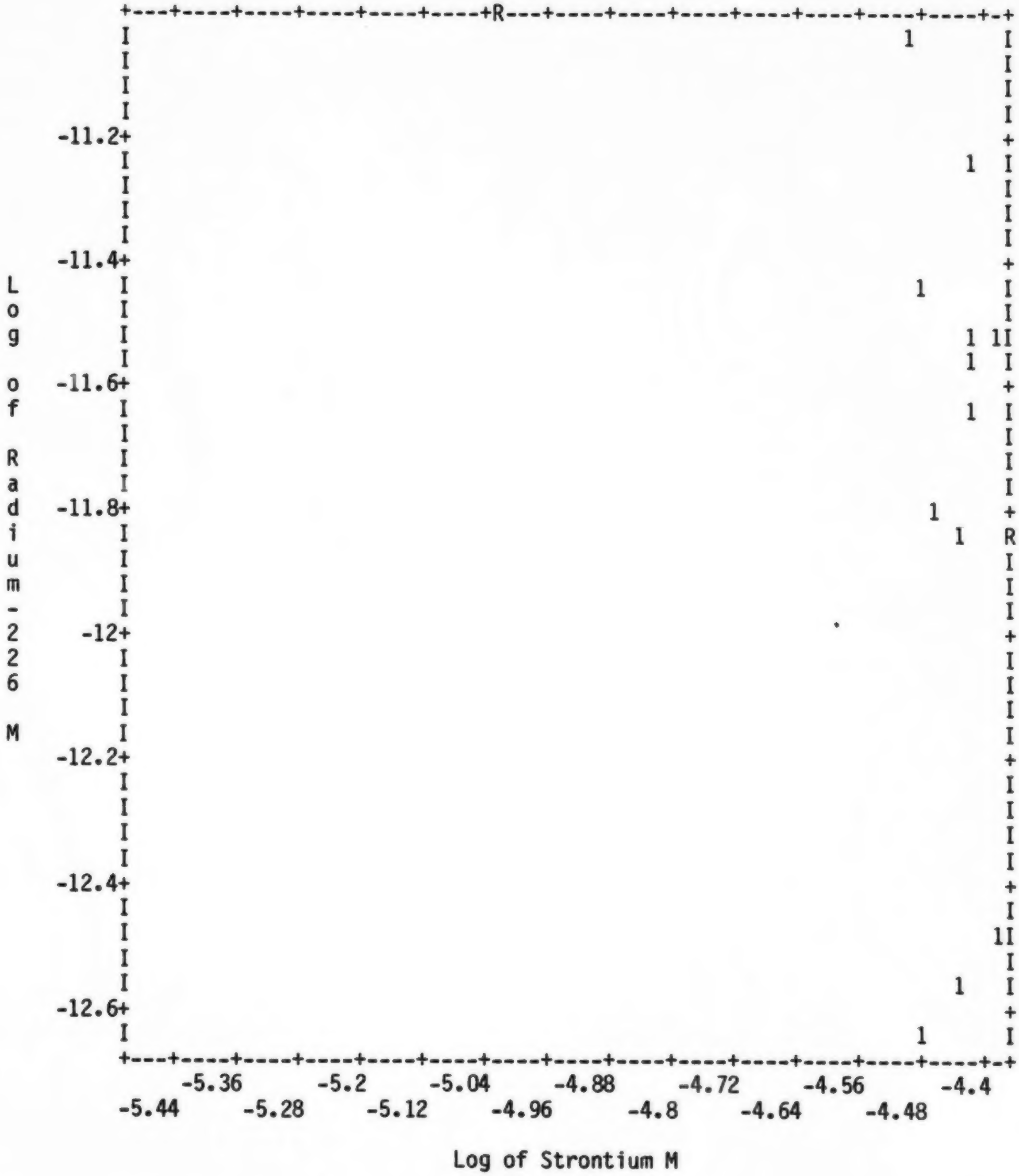
```
19 cases plotted. Regression statistics of CA on BA:
Correlation  .59486 R Squared  .35385  S.E. of Est     .54546 Sig.  .0072
Intercept(S.E.)     .94423(   .97051)  Slope(S.E.)     .53251(   .17452)
```

A.2(a) Plot of Ra with Ca from Leaching Liquor



```
12 cases plotted. Regression statistics of RA on CA:
Correlation -.19417 R Squared  .03770  S.E. of Est    .53484 Sig.  .5454
Intercept(S.E.)  -15.81380(  6.46478)  Slope(S.E.)   -2.28618(  3.65241)
```

A.2(b) Plot of Ra with Sr from Leaching Liquor



```
12 cases plotted. Regression statistics of RA on SR:
Correlation -.08966 R Squared  .00804  S.E. of Est     .54302 Sig.  .7817
Intercept(S.E.)  -17.31944( 19.49943)  Slope(S.E.)   -1.25180(  4.39713)
```

A.2(c) Plot of Ra with Fe from Leaching Liquor

```
         +--+----+----+----+----+----+----+----+----+----+----+----+----+----+--+
         I                                                                    1 I
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -11.2+                                                                      +
         I                                                                   1  I
         I                                                                      I
         I                                                                      I
         I                                                                      R
    -11.4+                                                                      +
L        I                                                                     1I
o        I                                                                      I
g        I                                                                  11  I
         I                                                                    1 I
o   -11.6+                                                                      +
f        I                                                                    1 I
         I                                                                      I
R        I                                                                      I
a        I                                                                      I
d   -11.8+                                                                 1    +
i        I                                                             1        I
u        I                                                                      I
m        I                                                                      I
-        I                                                                      I
2     -12+                                                                      +
2        I                                                                      I
6        I                                                                      I
         I                                                                      I
M        I                                                                      I
    -12.2+                                                                      +
         I                                                                      I
         I                                                                      I
         I                                                                      I
         I                                                                      I
    -12.4+                                                                      +
         I                                                                      I
         I                                                                1     I
         I                                                                      I
         I                                                                 1    I
    -12.6+                                                                      +
         I                                                             1        I
         +--+----+----+----+----+----+----+----+----+----+----+----+-R--+----+--+
       -2.16        -2     -1.84     -1.68     -1.52     -1.36      -1.2
            -2.08     -1.92     -1.76      -1.6     -1.44     -1.28     -1.12

                                     Log of Iron M

12 cases plotted. Regression statistics of RA on FE:
Correlation  .67133 R Squared  .45068  S.E. of Est     .40410 Sig.  .0168
Intercept(S.E.)   -2.38350( 3.27857) Slope(S.E.)    8.25728( 2.88282)
```

APPENDIX 3

Discussion of r^2

APPENDIX 3
DISCUSSION OF r^2

Bivariate linear correlation provides a single number which summarizes the relationship between two variables (Nie et al, 1975). A correlation coefficient (r) indicates the degree to which variation (or change) in one variable is related to variation (change) in another. A correlation coefficient not only summarizes the strength of association between a pair of variables, but also provides an easy means to compare the strength of relationship between one pair of variables and a different pair. Two parameters may be defined for bivariate correlation:

> r the Pearson coefficient or correlation coefficient, and
> r^2 the coefficient of determination.

As implied, one is a square of the other. Generally r^2 is used in this report because it describes the portion of the total variance which is explained by the correlation; the total variance is defined relative to the mean of the observations. Mathematically r^2 is defined as the ratio of the square of the covariation to the product of the variation in the two variables.

In formula form, r^2 is defined as:

$$r^2 = \frac{\left[\sum_{i=1}^{N} (X_i - \bar{X}) \quad (Y_i - \bar{Y}) \right]^2}{\left[\sum_{i=1}^{N} (X_i - X)^2 \right] \quad \left[\sum_{i=1}^{N} (Y_i - Y)^2 \right]}$$

Where X_i = i_{th} observation of variable X
Y_i = i_{th} observation of variable Y
N = number of observations

$\bar{X} = \sum_{i=1}^{N} X_i/N$ = mean of variable X

$\bar{Y} = \sum_{i=1}^{N} Y_i/N$ = mean of variable Y

In most research it is difficult to find a regression line, expecially a straight one, which perfectly fits the data. A measure of the "goodness of fit" is given by r. When there is a perfect fit (no error) the value is $\pm$ 1.0 and the sign depends on the direction of the slope. Similarly, a value of zero denotes the absence of a linear relationship.

Since r and r^2 are symmetric measures of association between two variables, it does not matter which variable is considered to be predicting the other unlike in the linear regression analysis. Both r and r^2 measure the strength of the linear relationship. However, the real strength of the relationship is best indicated by r^2, the proportion of variance of Y explained by linear regression of X. r^2 is essentially a measure of the total variance explained by a linear correlation between two variables. Therefore, r^2, is the proportionate reduction in variation due to fitting of a straight line through the data compared to using the mean of the data to describe the observations. Since r^2 is a proportion, it lies between zero and 1.0.

Values of r^2 can be judged on a relative basis (comparing correlation to correlation) or on an absolute basis (defining a minimum value for r^2 for a correlation to be judged acceptable). Colton (1974), suggests that the following crude "rule of thumb" may be useful as a general guideline. Values of r^2 between 0 and 0.13 indicate little or no relationship, those from 0.13 to 0.25 indicate a fair degree of relationship, those between 0.25 and 0.56 indicate a moderate relationship and those above 0.56 indicate a very good to excellent relationship. This crude "rule of thumb" is probably inadequate for instrumental data comparing duplicates, triplicates, etc., over a concentration range in QA/QC studies. This "rule of thumb" is suggested by an author whose field is the statistics of social sciences as applied to the medical field, a field in which both physical and social variation might cause one to expect lower values of r^2 as indicative of a good relationship. Notwithstanding these reservations, this rule of thumb is judged to be adequate for the experimental data obtained in this study.

APPENDIX 4

Model Development and Experimental Design

APPENDIX 4 MODEL DEVELOPMENT AND EXPERIMENTAL DESIGN

A4.1 Model Development

A tentative model, which we have done some thinking about, and which can explain some of the observations of this report and the conceptual model (Figure 3.1) is of the following form:

$$\frac{d}{dt}[U] = + r_{uo_2} A_{uo_2} \tag{1}$$

$$\frac{d}{dt}[Th] = + r_{ThO_2} A_{2ThO_2} \tag{2}$$

$$\frac{d}{dt}[Pb] = a_{UPb} r_{uo_2} A_{uo_2} + a_{ThPb} r_{ThO_2} A_{ThO_2} - k_{Pb}(C^S_{Pb} - [Pb])^{n1} \tag{3}$$

$$\frac{d}{dt}[Ba] = r_{BA} A_{BA} - k_{Ba}(C^S_{Ba} - [Ba])^{n2} \tag{4}$$

$$\frac{d}{dt}[Ra\text{-}226] = a_{URa} r_{UO_2} A_{UO_2} - \lambda_{RaBa} k_{Ba}(C^S_{BA} - [Ba])^{n2} - \lambda_{RaPb} \cdot k_{Pb}(C^S_{Pb} - [Pb])^{n1} \tag{5}$$

$$\frac{d}{dt}[Ra\text{-}228] = a_{ThRa} r_{ThO_2} A_{ThO_2} - \lambda_{RaBa} k_{Ba}(C^S_{BA} - [Ba])^{n2} - \lambda_{RaPb} \cdot k_{Pb}(C^S_{Pb} - [Pb])^{n1} \tag{6}$$

Here [ ] is the concentration of U, Th, Pb, Ba, Ra-226 and Ra-228 in solution, r is the dissolution rate constant per unit surface area (A), and the subscripts refer to the uranium (UO_2) and thorium minerals. The rate constant will be a function of pH, temperature and other solution variables. The coefficient "a" is a stoichiometric coefficient. For example, a_{UPb} of Eq. (3) refers to the stoichiometry of Pb:U in the dissolution of Pb from the uranium mineral. For the symbol, C^S, C^S_{Ba} for example, is the equivalent saturation solution concentration of Ba. The kinetic expression $(k_{Ba}(C^S_{Ba} - [Ba])^{n2}$, is the form often used to describe crystallization of barium sulphate in a 1:1 electrolyte of Ba^{2+} and SO_4^{2-}. It would need to be changed to reflect the much larger sulphate concentration relative to barium concentration, but it is conceptually useful for discussion purposes. The Doerner-Hoskins kinetic coefficient, λ, describes the amount of radium incorporated into the mixed crystal relative to the amount of host crystal formed. Whether the kinetic coefficient or equilibrium coefficient, D, describes the coprecipitation process awaits further evaluation.

DISCUSSION

In previous work, it was observed that smaller proportions of Ra-226 than of Ra-228 are found in solution after 24 hr of leaching. The above equations can explain this observation as follows. If the dissolution of a large proportion of uranium minerals and barium-containing minerals is quick (e.g., less than 30 min.), much of the Ra-226 and Ba would be recrystallized as a $(Ra, Ba)SO_4$ before substantial amounts of Ra-228 entered solution. If the barium concentration is much lower over the period of say 4 hr to 24 hr than over the first half hour, then the rate of recrystalization is lower because the difference $(C^S_{Ba} - [Ba])$ is smaller. If during this latter period most of the Ra-228 is entering solution, less of it would be crystallized than of Ra-226.

A similar process could occur for lead, if Ra-226 coprecipitation occurs with lead sulphate. Lead (Pb-206 as well as Pb-210) dissolves with Ra-226. from the uranium mineral. Pb-206 is the largest mass fraction. If it recrystallizes fairly fast, it will aid the removal of Ra-226 from solution before substantial amounts of Ra-228 enter solution. Furthermore, during the latter leaching time, if lead sulphate removes Ra-228 from solution, the lead sulphate containing Ra-228 may have substantively different Pb-206/Pb-208 rations than the lead sulphate containing Ra-226 because more of the lead in the latter crystal would be from dissolution of the Th-232 mineral containing Pb-208.

Another phenomenon implied in the definitional sketch but not explicity described in the equation is fluid films and diffusional differences. The sketch suggests that some minerals which leach and which contain Ra-226 may be positioned physically closer to the recrystallization site than others. Such films may be 5-10 um in thickness. In such films, the crystallization processes will be a function of local chemical characteristics, rather than bulk fluid characteristics. Also Pb-206 may crystallize near the uranium mineral and Pb-208 near the thorium mineral. Such a phenomena would suggest alteration of Eq. (3) to consider these differences. Experiments designed to evaluate these possibilities would be useful.

Possible Isotope Measurements

It is plausible, from the above discussion, that chemical dissolution techniques which are able to peel off the successive layers of lead sulphate formed over time and analysis of the leach water for the associations of Pb-206, Pb-208, Pb-210, Ra-226 and Ra-228 would give some answers to the above questions. It is also evident that chemical dissolution techniuqes which are able to differentially dissolve barium sulphate and lead sulphate are required. These would allow us to examine for whether barium sulphate or lead sulphate are host to most of the Ra-226, and the isotopes of Pb involved.

APPENDIX A4.2 ANALYSIS OF DISTRIBUTION FUNCTIONS

The equilibrium distribution coefficient D for (Ba, Ra)SO_4(s) is given by:

$$D = \frac{\dfrac{N_{RaSO_4(s)}}{N_{BaSO_4(s)}}}{\dfrac{(mRa^{2+})}{(mBa^{2+})}} \tag{7}$$

The Doerner-Hoskins (kinetic) coefficient, λ is given by

$$\lambda = \frac{\log \dfrac{(mRa_i^{2+})}{(mRa_f^{2+})}}{\log \dfrac{mBa_i^{2+}}{mBa_f^{2+}}} \tag{8}$$

Here, $N_{RaSO_4(s)}$ and $N_{BaSO_4(s)}$ are the molal fractions of Ra-226 and Ba in solid solution of the $BaSO_4(s)$ crystal, (mRa^{2+}) and (mBa^{2+}) are the molal aqueous concentrations in solution, and the subscripts i and f refer to the initial and final solution concentrations.

The historical approach has been to use known solution conditions to calculate the appropriate quantities and to conduct timed experiments in which an increasing amount of Ra and Ba is precipitated in a batch system. The model evaluation is presented in Figure B4.1 and B4.2 (Figure 6 and 7 from Appendix 1). Using solution concentrations (for λ) and solution-solid concentrations (for D), the appropriate coefficient (D or λ) is plotted against the percent of barium precipitated. The coefficient which is independent of the extent of barium precipitated means that it is the appropriate function to describe the data. In Figure B1, λ plots independent of barium precipitated while D is not. Hence, λ is the appropriate distribution function. In Figure B2 for another data set with the same ions but under different experimental conditions, D is independent of % barium precipitated; hence D describes the data set. Hence, subtles in experimental conditions have a large impact on the distribution functions. By analogy, we expect the same behaviour as a result of subtle changes in experimental conditions in the dissolution experiments.

In the case of a dissolution study, we do not have available information concerning the time history of solution characterisitcs which formed the solid, nor do we know the total amount on the precipitate until it is all dissolved. But analyzing the λ model allows insights into discriminating between λ and D. The λ model gives

$$\text{Log } mRa_i^{2+} - \text{Log } mRa_f^{2+} = (\log mM_i^{2+} - \text{Log } mM_f^{2+}) \tag{9}$$

which when rewritten becomes

$$\text{Log } mRa_f^{2+} = \text{Log } mM_f^{2+} + (\text{Log } mRa_i^{2+} - \text{Log } mM_i^{2+}) \tag{10}$$

If Ra_f^{2+} and M_f^{2+} in the leaching solution are viewed as influencing the initial portion dissolved from the solid in a washing study, and if Ra_i^{2+} and M_i^{2+} represents estimates of the total concentration in the leaching pachuca before precipitation and hence which correspond to the total which can be dissolved from the solid, dissolution should represent the reverse process of precipitation. Hence during dissolution of increasing amounts of barium and radium for example, a plot of cumulation amount of radium dissolved against the cumulative amount of barium dissolved should give a straight line on a log-log plot with a slope which is .

Such log-log plots have been obtained in this study in which increasing concentration of EDTA or other washing agents (e.g., KCl etc.) were used to extract Ra-226. Duplicate treatments (e.g., two of 10^{-4} M EDTA, two of 10^{-3} M EDTA) etc., were used for all treatments in early experiments. In the later experiments, single and duplicate treatments were used due to budget limitations. A summary of experimental replication is given in Table B4.1. The duplicates were generally quite close. They may allow separation of experimental variability from model variability. But in some experiments, more replication (e.g., duplicate treatments throughout, and occasionally triplicate treatments) and more treatments at different concentrations would have been useful to decrease the variance and to allow separation of model variance from experimental variance.

APPENDIX 5

Laboratory Facilities

APPENDIX 5 LABORATORY FACILITES

A5.1 Laboratory Methods of Analysis (Beak Laboratories)

Table A5.1 describes the operating characteristics of the methods. The majority of metals and elemental analysis is being done on the DCP instrument except for cold vapour flameless AA for mercury and selected metals including arsenic by hydride evolution - AA.

Atomic Absorption Spectrophotometers

- One Perkin-Elemer Model 303 and one Model 403 with hollow cathode and electrodeless discharge lamps; power supplies; and microcomputer interfaced and controlled.

- Enhancement of lower limits is achieved by solvent extraction, high energy electrodeless discharge lamps, and volatilization.

- Deuterium background correction available or known-addition technique to eliminate interference. Results displayed on Pet Computer as ppm and printed out.

Direct Current Plasma (DCP) Analyser

Beckman Spectraspan V Direct Current Plasma Analyser with a Spectrajet III DC argon plasma excitation source; two ten element cassettes for simultaneous determination of cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, silver, and zinc on one cassette and aluminum, barium, beryllium, calcium, magnesium, molybdenum, potassium, sodium, strontium, and vanadium on the other cassette; a single element cassette for sequential determination of any element (thorium, silicon, titanium); DBC-33 dynamic background compensator; microprocessor controlled RS-232C data interface; auto sampler interface; printer.

TABLE A5.1 ANALYTICAL METHODOLOGY SURVEY FORM OPERATING CHARACTERITICS OF METHODS

TYPE OF SAMPLE: Tailings:
Water Matrix (mg/L)
Solids Matrix (ug/g)

Parameter	Units of Measurement	Routine Analytical Operating Range		Best Method Lowest Reported Value	Method	Sample Preparation Laboratory Nomenclature	Bias (versus true value)	Literature Reference
		Upper	Lower					
pH	pH units	14	0	0.05 units	Meter	Probe	-	APHA 423
TIC	mg/L	50	1	0.5	Analyser	Filtered or not	Low	BOM1
Sulphate	mg/L	200	0.2	0.05	IC	Filtered, DIONEX	-	DOM
Chloride	mg/L	35	0.1	0.1	IC	Filtered, DIONEX	-	DOM
Silica	mg/L	100	0.1	0.05	DCP	Supernatant, acidified	?	BOM2
	ug/g	2,000	5	2				
Calcium	mg/L	400	0.2	0.05	DCP	Supernatant, acidified	-	BOM2
	ug/g	10,000	5	2				
Magnesium	mg/L	400	0.1	0.01	DCP	Supernatant, acidified	-	BOM2
	ug/g	10,000	5	2				
Barium	mg/L	400	0.01	0.005	DCP	Supernatant, acidified	-	BOM2
	ug/g	10,000	1	0.5				
Aluminum	mg/L	100	0.01	0.005	DCP	Supernatant, acidified	-	BOM2
	ug/g	2,000	1	0.5				
Potassium	mg/L	100	0.02	0.01	DCP	Supernatant, acidified	-	BOM2
	ug/g	2,000	2	1				
Strontium	mg/L	400	0.01	0.005	DCP	Supernatant, acidified	-	BOM2
	ug/g	10,000	1	0.5				
Sodium	mg/L	200	0.1	0.05	DCP	Supernatant, acidified	-	BOM2
	ug/g	10,000	5	2				
Lead	mg/L	100	0.02	0.005	DCP	Supernatant, acidified	high	BOM2
	ug/g	2,000	2	1				
Iron	mg/L	200	0.02	0.01	DCP	Supernatant, acidified	-	BOM2
	ug/g	5,000	2	1				
Titanium	mg/L	100	0.01	0.005	DCP	Supernatant, acidified	-	BOM2
	ug/g	2,000	1	0.5				
Thorium	mg/L	100	0.05	0.02	DCP	Supernatant, acidified	-	BOM2
	ug/g	2,000	5	2				

BOM1 - Beckman Operations Manual (TOC Analyser)
BOM2 - Beckman Operations Manual (DCP)
APHA - Standard Methods for the Examination of Water and Wastewater, 15th Ed.
DOM - Dionex Operations Manual

Anions are determined by Ion Chromatography (IC) backed up by colourimetric methods (APHA, 1983). Inorganic carbon is measured by means of a Beckman Model 915A TOC Analyser.

A5.2 Quality Assurance Program (BEAK Laboratories)

Definition

Quality assurance comprises all those planned and systematic actions that are necessary to provide adequate confidence in the results of a monitoring program. Quality control comprises those quality assurance actions that provide a means to control and measure the characteristics of measurement equipment and processes to established requirements.

Quality assurance is the total program for assuring the reliability of monitoring data. Quality control is the routine application of procedures for controlling the measurement process.

Emphasis and technique may vary, but quality assurance can be described and practiced in terms of aware personnel, proper instrumentation, analytical methods, quality control, record keeping and management support.

Analytical Reproducibility

Reproducibility in reporting results is generally limited by one of the following factors in order of increasing significance.

- electronic (instrument) noise observed under extreme range expansion,
- inability to observe small changes in reading because of insufficient range expansion,
- analytical noise, e.g., non-reproducible colour development or noisy reagent background, independent of sample preparation procedures,
- sample preparation noise, e.g., poor reproducibility after sample digestion,
- sample non-homogeneity,
- poor sampling or sample handling and preservation.

Quality control and performance evaluation attempt to minimize and quantify the data scatter resulting from the measurement process. In order to permit a data quality assessment, the following data base may be useful:

- results of duplicate analysis of samples split at the laboratory for use in assessing in-lab precision,
- results of duplicate samples (separately sampled, not split) submitted "blind" from the field or by research personnel (D. Singh) to the laboratory for use in assessing the additional effect of field activities and sample type, or perishability, on precision,
- results of duplicate samples where one would be analysed "blind" by the contract laboratory, and the other would be forwarded to a control laboratory.

Detection limit and precision statements are advisory in nature. Field and/or time variability usually do not permit application of these concepts to assist the data user in interpreting his results unless in fact analytical effects are limiting.

The stated values (Table A5.1) are achievable provided the ion distribution is in reasonable balance. If one species dominates in excess causing colourimetric or spectral interference, then suitable dilutions are necessary and may increase detection limit. Dilutions are also used to check for linearity.

Lower detection limits and lower method sensitivity (good precision and accuracy) require additional test runs on undiluted and/or spiked samples or may be enhanced by extraction/separation/concentration techniques. In some cases, the swamping effects cannot be overcome by procedures available to BEAK. In some cases, special methods may allow BEAK to go below the best stated detection limits.

If the data user requires better precision or lower detection limits, he should request whether the analytical system can be adapted to his needs. If not, replicate samplings or analyses may be needed since the standard deviation of an average is $1/\sqrt{n}$ better than the standard deviation of a single result. This approach is not very efficient, however, because 9 replicate analyses will improve precision and detection criteria only by 3 times.

Analytical Accuracy

Accuracy measures the amount of bias which has been found, relative to some absolute reference or established true value. If precision is sufficiently poor, bias will be difficult to detect or correct; however, its influence on averaged data will still be real and significant.

Analytical accuracy is determined by processing calibration and test reference materials at the same time the routine samples are analysed. It has been found that standards used to produce calibration curves and samples to be analysed must have similar matrices to ensure that the instrument responses are similar for the interferences from the matrix. Reference materials are used for certain parameters that normally may need correction to adjust for bias.

Interlaboratory Studies

BEAK experience has shown that quality assurance programs must monitor internal laboratory performance on a continuous basis to ensure accurate and reproducible data. The following routine procedures may be included in analytical studies.

- Use certified and standard reference materials. Suitable standards will be obtained if necessary for the work.
- Use EPA reference solutions as secondary standards to check on bias.
- Process internal replicates.
- Process blind replicates.
- Carry out spiking to eliminate interferences and confirm recovery.
- Balance the anion and cation ratio (if applicable).

- Interlaboratory cross-checks. Several external checks are carried out each year and this information is used to monitor precision of methods and any creeping bias. This information is available if requested.

BEAK has participated in various independent and project-related interlaboratory studies. The following summarizes these programs. Complete documentation is available for inspection at the BEAK facilities.

Environment Canada Canada Centre for Inland Waters Burlington, Ontario	The National Interlaboratory Quality Control Program Continued participation since 1975. Studies 14, 15, 16, 18, 19, 20, 21 22, 23, 25, 27, 28, 29, 30, 33. DQC-2, DQC-3, LRTAP9, LRTAP10.
Environment Canada Fisheries and Oceans Capitaine Bernier Laboratories Longeuil, Quebec	Project Analytical Cross-Check Program Interlaboratory comparison of mercury, cadmium, copper, lead, selenium, and zinc in fish tissue in 1977. Interlaboratory comparison of cadmium, mercury, lead and PCBs in sediment and biological material in 1980.
Environment Canada Environmental Protection Service Bedford Institute of Oceanogrpahy	Project Analytical Cross-Check Program Interlaboratory comparison of mercury, cadmium, copper, and PCBs in sediment and biological material in 1980. Quality control check for PCBs, chlorobenzenes and PAHs in standards and spiked sediment.
Ontario Ministry of Environment Environment Laboratory Services Branch Toronto, Ontrio	Leachate Analysis Comparative Study 1985 Interlaboratory comparison of 5 industrial waste samples using the MOE Leachate Procedure (LP) for recovery of Cd, Cu, Cr, Mn, Ni, Pb and Zn.

National Research Council of Canada Ottawa, Ontario	Marine Analytical Chemistry Standard Program First Intercomparison Exercise for Trace Metals in Marine Sediments - NRC MS1/TM Calibration for Cu, Zn, Cd, Hg and Pb in 1984.
Energy, Mines and Resources Earth Sciences Geological Survey of Canada Ottawa, Ontario	Canadian Certified Reference Materials Project 1984 Collaborative testing of 4 stream sediments and 4 lake sediments for Hg, Cd, Cu, Cr, Fe, Ni, Pb, and Zn.

Typical results of BEAK participation in interlaboratory programs are given in Cheam and Chau (1985).

Reference Materials

The following lists reference materials that have been used in the laboratory.

Albacore Tuna Research Material 50
    National Bureau of Standards

Bovine Liver Standard Reference Material 1577
    National Bureau of Standards

Orchard Leaves Standard Reference Material 1571
    National Bureau of Standards

River Sediment Standard Reference Material 1645
    National Bureau of Standards

Sulphur in Residual Fuel Oil Standard Reference Material 1622a
    National Bureau of Standards

Oyster Homogenate MA-M-1
International Atomic Energy Agency

Fish Homogenate MA-M-2
International Atomic Energy Agency

Fish Tissue
Freshwater Institute, Winnipeg, Canada

Marine Sediments CS-1, HS-1, HS-2
National Research Council, Canada

Interlaboratory Study Sediment for PNAs EC-1, EC-2
Environment Canada

PCB in Sediment GROUP 1-978, 2-978, 3-978
USEPA

Marine Sediment MESS-1, BCSS-1
National Research Council

Municipal Digester Sludge
USEPA

Marine Sediments MS1/TM
National Research Council

Mine Tailings NUTP UTS-2, UTS-4
National Uranium Tailings Program

Urban Particulate Matter Standard Reference Material 1648
National Bureau of Standards

Trace Metals in Fish
USEPA

Note: Normally suitable reference materials are obtained for the specific needs of a project.

Summary of Internal Quality Assurance Program Used in this Study

For solids, a reference standard (CANMET tailings UTS-1 to UTS-5 or appropriate standard) was analysed for every twenty samples. For liquids, standard solutions for cations and anions of interest were analyzed every 15 to 20 samples. The DCP was calibrated daily. Electroneutrality balances were made on solutions where possible. An acceptable standard are judged to be ± 10% in concentrated waters and ± 20% in dilute systems.

A5.3 Laboratory Methods of Analysis (Monenco)

All samples were analysed according to the procedures outlined in the "Analytical Methods Manual-National Uranium Tailings Program" by Dean and Chiu, 1984 (see Section 5.3 and 5.4). They are in summary:

Radium-226, Radium-223 - High Resulution Alpha Spectrometry (HRAS) (BA-133 Tracer).

Th-232, Th-230, Th-228 - HRAS (Th-234 tracer).

Radium-228 - indirect measurment of daughter, Actinium 228, a beta emitter.

Lead-210 - indirect measurement of daughter, bismuth-210, a beta emitter.

Polonium-210 - HRAS (Po-208 tracer).

Uranium - delayed neutron activation (solids), fluorimetry (liquids).

Uranium Ratio
(U-234, U-234, U-238) - HRAS (after isolation of uranium).

A5.4 Quality Assurance Program (Monenco)

The Monenco quality assurance program for radiochemistry of solids involves the analysis of a CANMET standard (either standard tailing (UTS-1 to UTS-5) or standard ore (e.g., DL-1, DL-2, etc.) for every twenty field samples analysed. For liquids, standard solutions of the radioisotopes of interest are analysed at the same frequency. In addition, tha alpha spectrometers, gamma spectrometers and beta spectrometers are calibrated daily. A more detailed description of the quality assurance program is given below.

MONENCO ANALYTICAL LABORATORIES

MONENCO ANALYTICAL LABORATORIES - QUALITY CONTROL PROGRAM

The purpose of this quality control program is to assure the scientific reliability of the laboratory data. We use management, administrative, statistical, investigative, preventive and corrective techniques to maximize reliability of the data.

1.0 QUALITY CONTROL

1.1 Publication and distribution of current and complete analytical methods and procedures and analytical instrument operating instructions.

1.2 Distribution and retention of laboratory reports with provision for administrative technical review.

1.3 Quality control checks on analytical instruments to ensure proper function at all times.

1.4 A Preventive Maintainence Program.

1.5 A total analytical quality control system to ensure continued precision and accuracy of laboratory results. This includes:

- a) daily calibration (instrument standards),
- b) where available, control samples included with each run. A control sample is one that has a similar matrix and has a working value established by organizations such as ASTM or APHA,
- c) when a control sample is not available, a previously run unknown is included as a blind check sample,
- d) a reagent blank is analysed for all parameter determinations,
- e) if the results attained for the standard, control or recycle samples are not within acceptable established limits, the entire batch of analyses are repeated and control verified before reports are issued,
- f) policy (e) is based on the presence of large enough samples. When such is not the case two options will be available:
  - (i) non acceptance of the analysis by the laboratory, or
  - (ii) waiving of the quality control actions by the client.

1.6 Participation in inter-laboratory quality evaluation programs.

1.7 All personnel trained and qualified in quality control techniques prior to running new analyses.

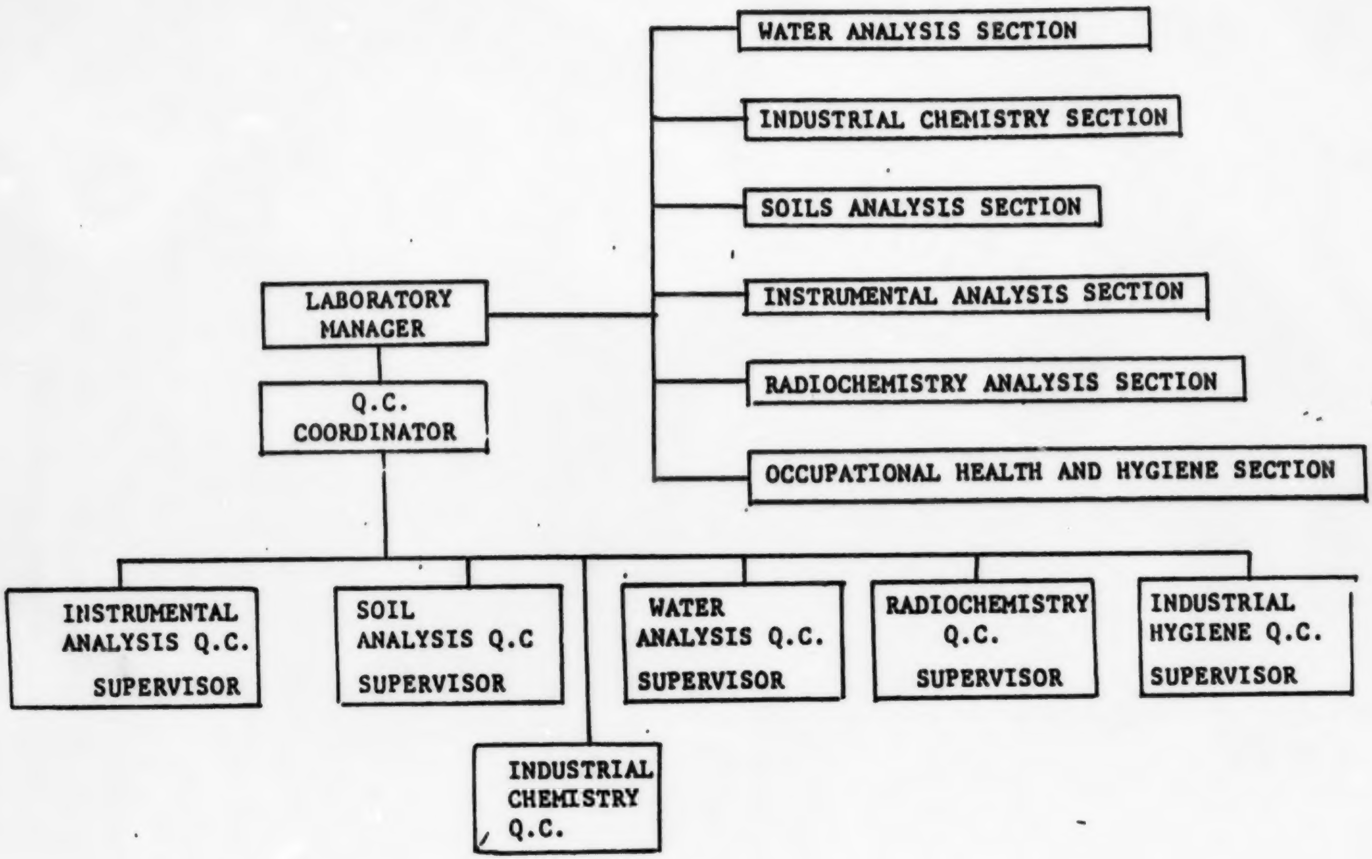

LABORATORY MANAGER
WATER ANALYSIS SECTION
INDUSTRIAL CHEMISTRY SECTION
SOILS ANALYSIS SECTION
INSTRUMENTAL ANALYSIS SECTION
RADIOCHEMISTRY ANALYSIS SECTION
OCCUPATIONAL HEALTH AND HYGIENE SECTION
Q.C. COORDINATOR
INSTRUMENTAL ANALYSIS Q.C. SUPERVISOR
SOIL ANALYSIS Q.C SUPERVISOR
INDUSTRIAL CHEMISTRY Q.C.
WATER ANALYSIS Q.C. SUPERVISOR
RADIOCHEMISTRY Q.C. SUPERVISOR
INDUSTRIAL HYGIENE Q.C. SUPERVISOR

Figure 1 LABORATORY QUALITY CONTROL OGRANIZATION

ORGANIZATION

Figure 1 shows the organization of the quality control program. The quality control coordinator reports to the lab manager. Each section has its own quality control program and is under the administration of the coordinator.

2.1 Duties of Coordinator

2.1.1 Responsibility for Q.C. program and for taking or recommending Q.C. measures to ensure accuracy and precision of data produced.

2.1.2 Developes statistical procedures and techniques and supervises their use.

2.1.3 Seeks out and evaluates new ideas in Q.C.

2.1.4 Monitors Q.C. program.

2.1.5 Advises lab manager in reviewing technology methods and equipment with respect to Q.C. aspects.

2.1.6 Recommends laboratory safety and occupational hygiene measures.

2.2 Duties of Q.C. Supervisor

2.2.1 Carry out monitoring, record keeping, statistical techniques and other functions required.

QUALITY CONTROL OPERATING PRINCIPLES

3.1 Record Keeping

The program endeavors to establish acceptable Q.C. records. Each sample is assigned a laboratory number and the analysis parameters requested are tabulated in a log book.

3.2 Reporting Practice

Each analysis report is prepared in triplicate. One copy is sent to the client and the other copies are filed in correspondence out and the specific project file. All raw data used to calculate each parameter is filed and stored in locations dedicated to that parameter and is retained for a period of two years. This practice allows rechecking of measurement data and calculation should it be necessary. Where possible, the estimated precisions of all data are included. Data obtained for standard reference materials and duplicates are also

3.3 Sample Storage

When available, each sample is retained in storage for a period of two years.

3.4 Instrument Calibration

A detailed plan is available to control the accuracy of measuring by use of calibration standards. Prior to the mesurement of a parameter for a batch of samples the instrument and method is calibrated using appropriate dilutions of certified standard solutions or sources. Each calibration standard is prepared in using a certified written procedure. The calibration procedure and measurement methodology is documented for reference purposes.

3.5 Calibration Interval

Each method and instrument is calibrated with solutions prepared using certified calibration standards each time a batch of samples are analysed and not less frequently than once per day. This interval is based on the degree of usage. The laboratory maintains all data and historical records pertaining to the calibration and maintenance of the instrumentation.

3.6 Environmental Conditions

All measurements and calibrations are carried out in an area that provides control of environmental conditions to the degree necessary to ensure required accuracy. The area is free of dust, vapours and vibration. Each instrument is not located close to equipment that produces vibration, chemical emissions or noise. The laboratory area is maintained at a temperature of 21-22°C. The analytical balances and electronic equipment for radiochemistry and the ICP-ES unit, for trace elements measurement, are located in an air conditioned environment. A filter air supply is provided to this area.

3.7 Preventive Maintenance

A preventative maintenance program is in effect that includes cleaning, lubricating, adjusting and testing of all instruments on a regular basis. Its purpose is to increase measurement system reliability and thus increase data completeness. A preventative maintenance schedule calling for visual and electronic examination of the instrumentation is presently in effect.

3.8 Use of Standard Reference Materials

When available, this laboratory makes use of NBS or comparable SRM. These materials, containing known amounts of measured parameters, also possess matrices as close as possible to those of the unknown samples. A SRM is placed in the sample analysis scheme at the time of sample logging and comprises 5% of all samples analysed (i.e., one out of every twenty samples is a SRM). In circumstances where reasonable agreement between the known and found composition of the SRM is not obtained, then all samples analysed in that batch are reanalysed. Agreement is obtained prior to reporting of data. In circumstances where SRM's are not available 5% of each sample batch are reanalysed and a sample that has been previously analysed and reported is substituted for the SRM.

3.9 Interlaboratory Testing Programs

This laboratory participates in interlaboratory testing programs organized by:

1) Environment Canada, 2) Alberta Environment, 3) Saskatchewan Environment, 4) Western Enviro-Agricultural Laboratories Association, 5) U.S. EPA, and 6) CANMET.

These proficiency testing procedures provide detailed information on how well the laboratory is able to perform.

A5.5 Quality Assurance Program for Overall Experimental Program

The internal quality assurance program of the laboratories is summarized above. It includes the following:

1. Experience in Inter Laboratory Comparison.
2. Internal Laboratory Quality Control Program/Routine Procedures.
3. Reference Materials Used.

External quality Control was also used. It consisted of using duplicate treatments in many experiments, triplicates in a few, and single treatments in the remainder. A summary of the replication is given in Table A5.3 as well as sample results of the replication.

TABLE A5.3: VALUES OF PARAMETERS FROM DUPLICATE EXPERIMENTS

Number	Ca	Ba	Sr	Fe	Pb	Ra-226
EDTA Solution	111,102	0.12,0.10	0.22,0.29	0.24,0.08	15,14.9	8.8,8.0
	124,269	1.16,4.5	0.59,1.10	28,31	48,54	330,550
	151,304,301	10.2,16.0	0.69,1.13,1.14	61,66,62	89,90,91	1662,1808,1710
	2.0,1.22	3.3,3.2	0.11,0.09	10.6,10.8	17,16.5	270,278
	8.1,6.6	4.0,4.0	0.36,0.35	87,87	35,34	611,524
	11.5,10.3	5.2,5.0	0.43,0.41	94,110	36,36	1341,1354
Distilled Water	1.15,1.25	0.31,0.30	0.10,0.11	3.6,3.6	8.3,8.6	54.9,60.5
	2.1,1.9	0.38,0.25	0.12,0.14	3.5,3.8	3.8,6.7	46,25
	620,640	0.03,0.04	0.34,0.71	0.14,0.06	0.21,0.18	2.2,1.
KCl Solution	7.6,9.0	1.0,1.0	1.4,1.4	11.2,14.3	66,66	243,279
	4.9,4.7	1.3,1.1	1.2,0.2	1.80,1.85	19.0,17.2	393,414
	17,17	4.2,3.8	0.6,0.5	1.25,1.10		1690,1708
	9.5,7.4	1.8,2.1	0.2,0.2	.05,.05	13.4,17.0	339,480
$CaCl_2$ Solution	35000,33000	7.0,7.0	31,31	10.1,10.8	112,116	1616,1464
	39,44	0.50,0.49	0.15,0.16	4.7,4.5	12.1,12.4	78.3,90
	38000,42200	6.5,6.8	7.8,8.1	8.5,9.9	106,113	1362,1504
$FeCl_3$	2.0,3.3	5.3,5.3	0.3,0.3	48000,50000	128,122	1807,2071
$BaCl_2$ Solution	1.85,1.90	14.4,15.6	0.14,0.10	6.0,3.9	9.2,8.4	45.6,73
	2.0,2.1	82,82	0.15,0.15	4.8,4.2	13.9,15.1	225,259
		1280,1270	0.48,0.50	6.1,6.5	41,40	924,849

TABLE A5.3: VALUES OF PARAMETERS FROM DUPLICATE EXPERIMENTS

Number	Ca	Ba	Sr	Fe	Pb	Ra-226
HCl Solution	1.92,2.3	0.27,0.28	0.21,0.22	7.0,7.8	24,24	42,41
	2.4,2.5	12.2,11.3	0.61,0.61	11.7,11.8	92,93	1985,1854
$HClO_4$ Solution	2.4,2.7	10.9,12.1	0.57,0.63	9.4,10.2	88,98	1968,2207
HNO_3 Solution	2.2,2.1	11.6,8.9	0.60,0.61	230,340	106,110	1921,1357
H_2SO_4 Solution	1.30,1.15	0.02,0.02	0.07,0.07	12.3,12.9	3.6,3.3	11.3,3.4
$HClO_4$:Acid Attack	1400,1600	0.8,0.9	1.0,1.2	620,640	57,58	428,424
	1500,1500	0.8,0.8	1.3,1.3	760,750	68,70	383,391
	1400,1500	4.4,4.3	1.5,1.6	990,890	98,95	917,848
HNO_3:Acid Attack	1260,1300	0.9,0.8	1.5,1.4	9000,8900	120,133	123,186
	1300,1300	3.6,3.7	1.7,1.7	8000,8000	139,136	710,573
H_2SO_4:Acid Attack	85,64	0.1,0.1	0.3,0.3	650,650	5.8,5.9	83,56
	66,90	0.2,0.2	0.3,0.4	1130,960	7.0,7.3	52,30